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Article

Sustainable solid-state synthesis of uniformly distributed PdAg alloy nanoparticles for electrocatalytic hydrogen oxidation and evolution

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ABSTRACT

New sustainable syntheses based on solid-state strategies have sparked enormous attention and provided novel routes for the synthesis of supported metallic alloy nanocatalysts (SMACs). Despite considerable recent progress in this field, most of the developed methods suffer from either complex operations or poorly controlled morphology, which seriously limits their practical applications. Here, we have developed a sustainable strategy for the synthesis of PdAg alloy nanoparticles (NPs) with an ultrafine size and good dispersion on various carbon matrices by directly grinding the precursors in an agate mortar at room temperature. Interestingly, no solvents or organic reagents are used in the synthesis procedure. This simple and green synthesis procedure provides alloy NPs with clean surfaces and thus an abundance of accessible active sites. Based on the combination of this property and the synergistic and alloy effects between Pd and Ag atoms, which endow the NPs with high intrinsic activity, the PdAg/C samples exhibit excellent activities as electrocatalysts for both the hydrogen oxidation and evolution reactions (HOR and HER) in a basic medium. Pd₉Ag₁/C showed the highest activity in the HOR with the largest $j_{0,m}$ value of 26.5 A g_{Pd}⁻¹ and $j_{0,s}$ value of 0.033 mA cm_{Pd}⁻², as well as in the HER, with the lowest overpotential of 68 mV at 10 mA cm⁻². As this synthetic method can be easily adapted to other systems, the present scalable solid-state strategy may open opportunity for the general synthesis of a wide range of well-defined SMACs for diverse applications.

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1. Introduction

Supported metallic alloy nanocatalysts (SMACs) have sparked tremendous interest in industry and fundamental research due to their high intrinsic activity, stability, and recyclability. For example, SMACs have been widely applied in the fields of thermal and electrochemical catalysis [1–3]. In particular, alloying two metals enable tailoring of their electronic

or/and geometric structures and can induce a synergetic catalysis effect, thus enhancing the intrinsic activity of the active sites or/and modifying the reaction routes to speed the reactions [4,5]. Additionally, reducing the size of alloyed nanoparticles (NPs) and improving their dispersion on supports can endow SMACs with a larger number of accessible sites, which guarantees the presence of sufficient active centers for catalytic reactions. However, the high surface energy of NPs and the

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difficulty of alloying metals with different physical/chemical properties often result in severe aggregation and inhomogeneous alloying of NPs. Consequently, the development of efficient strategies to produce small-sized, well-dispersed alloy NPs for SMACs is of considerable importance.

In recent years, various solution-based strategies to produce SMACs, including co-precipitation, impregnation, and solvothermal/hydrothermal methods, have been widely explored [6–8]. To effectively control the size and avoid the potential agglomeration of alloy NPs, large amounts of organic agents (e.g., organic solvents, surfactants, and capping agents) were generally and largely introduced in the synthesis procedures. However, this makes the entire process cost-ineffective, complicated, and environmentally unfriendly; thus, SMACs produced in this manner are unfavorable for large-scale applications. Moreover, the organic agents, especially surfactants, are likely to be strongly adsorbed on the surface of the alloy NPs, thus decreasing their catalytic surface areas. The extra steps required to remove these ligands unavoidably cause sintering of the alloy NPs, which decreases their active surface areas and amount of accessible active sites for catalytic applications.

To overcome these drawbacks, solid-state strategies have been explored as alternative methods to produce SMACs in recent years. The typical solid-state strategy of high temperature pyrolysis has been employed to produce many types of SMACs; however, control of the morphology and size of the alloy NPs is very difficult at high temperature because of their high surface energy. To achieve morphological control and limit overgrowth of the alloy NPs, the pyrolysis must be completed within a short reaction time using special heating equipment [9]. In light of these drawbacks, the use of mortar-pestle milling for the synthesis of NPs has attracted considerable attention, as this method can be carried out under normal ambient conditions and can eliminate or dramatically reduce the usage of hazardous organic agents [10–13]. However, to date, strategies for the synthesis of small-sized alloy NPs that are uniform dispersed on matrices via mortar-pestle milling have rarely been reported, and remain a great challenge.

Herein, a series of carbon-supported PdAg alloy NPs were produced using a mechanochemically assisted strategy involving the direct mortar-pestle milling of the precursors in an agate mortar at room temperature. The resulting PdAg alloy NPs exhibited a small size and clean surfaces and were highly and uniformly distributed on a carbon matrix, thus providing abundant accessible active sites. By adjusting the atomic ratio of Pd and Ag through tuning the amounts of the precursors, the optimal positive synergistic and alloy effects were easily realized to produce PdAg alloy NPs with a high intrinsic activity. Because of these features, the resulting PdAg/C electrocatalysts showed excellent activities for the hydrogen oxidation and evolution reactions (HOR, HER) in an alkaline medium. Notably, neither the size nor the dispersion of the alloy NPs was influenced by the topological structure of the carbon support, and thus, their use could be extended to most nanocarbons, including super P, 3D graphene, and self-prepared 3D porous carbon. The developed strategy was quite simple, time-efficient, and environmentally friendly, and thus represents a new way to

produce ultrafine and highly-dispersed alloy NPs on matrices for various catalytic applications.

2. Experimental

A series of carbon-supported PdAg alloy NPs were synthesized by directly grinding the precursors in an agate mortar at room temperature. Please see more details in the Supporting Information.

3. Results and discussion

The procedure for the synthesis of PdAg/C via the mechanochemically assisted strategy involving mortar-pestle milling is illustrated in Fig. 1. In a typical synthesis, the metal precursors (palladium chloride and silver nitrate) were uniformly mixed with carbon black, sodium hydroxide (NaOH), and sodium borohydride (NaBH_4) via mortar-pestle milling. With the assistance of NaOH, the metal precursors were gradually reduced by NaBH_4 to form PdAg alloy NPs, which were loaded on the carbon support in significant amounts. The final products were easily obtained after the removal of impurities via rinsing with water. The carbon-supported PdAg alloy products with different molar ratios of Pd/Ag were denoted as Pd/C, $\text{Pd}_9\text{Ag}_1/\text{C}$, $\text{Pd}_5\text{Ag}_5/\text{C}$, $\text{Pd}_1\text{Ag}_9/\text{C}$, and Ag/C, respectively.

The morphologies of the PdAg/C and reference samples were first analyzed using transmission electron microscopy (TEM). As shown in Figs. 2(a)–(d) and 3(a),(b), the dispersion of NPs gradually improved with increasing Ag content, and the NPs of $\text{Pd}_5\text{Ag}_5/\text{C}$ showed the best dispersion. Further increasing the Ag content led to deterioration of the dispersion of the NPs. The corresponding bar graphs reveal that the NPs of Pd/C, $\text{Pd}_9\text{Ag}_1/\text{C}$, $\text{Pd}_5\text{Ag}_5/\text{C}$, $\text{Pd}_1\text{Ag}_9/\text{C}$, and Ag/C had average sizes of 4.8, 5.3, 4.9, 4.5, and 4.7 nm, respectively (Figs. 2(e)–(h) and 3(c)). These results indicated that the composition of the NPs had a negligible influence on their size. The fringe spacings for the NPs of Pd/C and Ag/C can clearly be distinguished in the insets of Fig. 2(a),(d), and were indexed to the (111) plane of metallic Pd and Ag, respectively. The lattice spacings in the insets of Figs. 2(b),(c) and 3(b) were measured to be 0.230, 0.233, and 0.231 nm, respectively, all of which were intermediates between the lattice spacings of the (111) plane of metallic Ag (0.24 nm) and Pd (0.22 nm), indicating successful PdAg

Fig. 1. Schematic illustration of the synthesis of PdAg/C.

Fig. 2. TEM images and particle size distributions of Pd/C (a, e), Pd₉Ag₁/C (b, f), Pd₅Ag₅/C (c, g), and Ag/C (d, h). Insets in a–d are the HRTEM images of the corresponding NPs.

alloying in the Pd₉Ag₁/C, Pd₅Ag₅/C, and Pd₁Ag₉/C samples [14,15]. As a typical sample, Pd₅Ag₅/C was further analyzed using scanning TEM (STEM) and the energy-dispersive spectrometry (EDS) mapping technique. As shown in Fig. 3(d)–(g), the elements Pd and Ag were finely distributed across the carbon matrix. Based on the above results, it can reasonably be concluded that PdAg alloy NPs with an ultrafine size and high dispersion on the carbon matrix were successfully synthesized via our developed mortar-pestle grinding strategy, and that

their composition could be tuned by simply adjusting the molar ratio of the precursors.

The chemical composition and crystal structure of the PdAg/C and reference samples were characterized using X-ray diffraction (XRD); the results are shown in Figs. 4(a) and S1. In addition to the two characteristic peaks of the carbon matrix at 24.6° and 44.1°, several intense diffraction peaks corresponding to Pd, PdAg, or Ag NPs were clearly observed. The diffraction peaks at 40.12°, 46.66°, and 68.12° in the Pd/C sample

Fig. 3. (a, b) TEM images of Pd₅Ag₅/C (Inset in b is the HRTEM image of the corresponding NPs); (c) Corresponding particle size distribution; STEM (d) and EDS mapping images (e–g) of Pd₅Ag₅/C: (e) C, (f) Pd, and (g) Ag.

Fig. 4. XRD patterns (a), XPS survey spectra (b), Ag 3d (c), and Pd 3d (d) XPS spectra of the as-prepared and reference samples.

corresponded well with the (111), (200), and (220) planes of Pd metal (JCPDS No. 46-1043), respectively. The characteristic peaks at 38.12°, 44.28°, and 64.43° detected in the Ag/C sample were ascribed to the (111), (200), and (220) planes of Ag metal (JCPDS No. 04-0783), respectively. For the alloy samples, the main peaks shifted slightly toward higher angle compared to those of Ag metal, which can be mainly attributed to the alloy effect [16]. Since the atomic radius of Pd (137 pm) is smaller than that of Ag (144 pm), shrinkage of the nanoalloyed phase would be expected to occur with increasing Pd content, which would cause the peaks of the XRD patterns shift to a higher angle [17,18]. These results again indicated that PdAg alloy NPs were successfully prepared via our developed mortar-pestle grinding strategy, in agreement with the TEM observations.

X-ray photoelectron spectroscopy (XPS) was employed to characterize the surface composition and chemical states of the PdAg/C and reference samples. Fig. 4(b) shows the XPS survey spectra. Only the elements Pd and C or Ag and C were detected in Pd/C and Ag/C, respectively, whereas Pd, Ag, and C were clearly observed in the Pd₉Ag₁/C, Pd₅Ag₅/C, and Pd₁Ag₉/C samples, indicating the successful fabrication of bimetallic samples. Fig. 4(c) and (d) show the Ag 3d and Pd 3d core level spectra. Compared to those in the Ag/C spectrum, the Ag 3d core-level peaks were clearly shifted to lower binding energies in the three alloy samples. The magnitude of this shift became greater with increasing Pd content (Fig. 4(c)). In the Pd 3d XPS spectra, however, the binding energies of three alloy samples were shifted to higher binding energy compared to those of Pd/C (Fig. 4(d)), with the Pd 3d binding energy becoming more positive with increasing Ag content. The effect of negatively charged Ag and positively charged Pd in the PdAg alloy were in good agreement with previous reports in the literature, which attribute this phenomenon to the *d*-band overlap of Pd and Ag atoms, and, thus, electron transfer from Pd to Ag [19–21]. These results again demonstrated the successful preparation of PdAg alloy NPs via our developed mortar-pestle milling strategy.

To understand the mechanism by which the small-sized, highly dispersed PdAg alloy was formed during the mortar-pestle milling, a control sample was synthesized using the same procedure as for Pd₅Ag₅/C, except that NaOH was not added. Notably, large-sized NPs (9.74 nm) with some aggregation were detected on the carbon matrix, as demonstrated by their TEM images and XRD patterns (Figs. S2 and S3). The corresponding HRTEM image shows a crystalline lattice fringe with a lattice spacing of 0.231 nm, confirming the successful formation of the PdAg alloy NPs. These results indicated that the addition of NaOH during the synthetic process played a critical role in controlling the size of the PdAg alloy NPs rather than affecting their crystal structure. The importance of NaOH in the synthetic process was ascribed to the following factors: (1) Metal ions often coordinate with OH⁻ to form mixed M-OH intermediates with reduced redox potentials, which thus retard the redox reaction rate between the M-OH intermediates and NaBH₄, leading to the formation of small-sized PdAg alloy NPs on the carbon matrix [10,22]. (2) NaOH can also activate the carbon matrix during the mortar-pestle milling, endowing the

carbon matrix with abundant oxygen-based groups, e.g., C=O species (Fig. S4). The oxygenated functional groups can strongly stabilize the newly formed PdAg alloy NPs and largely prevent their overgrowth, allowing them to maintain their ultrafine size on the carbon matrix. Additionally, the dispersion, which represents the fraction of exposed active metal atoms on a catalyst, can be roughly determined using the average size of metal NPs [23,24]. Thus, the ultrafine size of the PdAg alloy NPs promoted their high dispersion on the catalyst. This indicates that during the synthetic process, NaOH either controls the dispersion of PdAg alloy NPs on the carbon matrix. Notably, no post-treatment was applied to the carbon matrix in this work to synthesize the supported PdAg alloy NPs. Thus, it was surmised that other carbon materials, such as conductive carbon black, 3D graphene, super P, and self-prepared 3D porous carbon, could be used as matrices for the NPs. As expected, three Pd₅Ag₅/C samples were successfully prepared using these carbon materials as the matrix; the PdAg alloy NPs on these matrices had sizes of 4.3, 3.6, and 3.5 nm and were highly dispersed (Figs. S5–S8). Based on these results, it can reasonably be concluded that the topological structure of the carbon matrix has little influence on the size and distribution of PdAg alloy NPs.

The electrocatalytic HOR and HER in alkaline electrolytes are the subject of extensive investigation, as these reactions are the key steps in alkaline fuel cells and water splitting, respectively. Because of their high intrinsic activities, Pt-based materials are ideal catalysts for both the HOR and HER. However, their practical application has been hindered by the limited availability and high cost of Pt [25–30]. To overcome this problem, the development of various affordable Pt-free catalysts with high performance is of great significance, but remains a challenge. Pd-based materials have been widely reported as substitutes for Pt-free catalysts and have attracted great attention in recent years. Unfortunately, to date, their electrocatalytic activity for the HOR and HER have been far lower than that required for actual applications. Consequently, the HOR and HER were selected as model reactions to explore the electrocatalytic activity of the developed PdAg/C catalysts in this work.

First, the HOR electrocatalytic activity of PdAg/C samples with a Pd mass loading of 10 $\mu\text{g}_{\text{Pd}} \text{ cm}^{-2}$ was explored in 0.1 M KOH solution using a standard three-electrode system at room temperature. As shown in the *iR*-corrected HOR polarization curves collected at different rotation speeds in Figs. S9(a), S10(a), and S11(a), the anodic current increased as the rotation speed was increased from 400 to 1600 rpm, indicating that the HOR for these samples was triggered via mass-transfer related anodic current [31]. Importantly, it is the Pd in the alloy samples that determines their HOR activity. Therefore, only the three Pd-enriched samples (Pd/C, Pd₉Ag₁/C, and Pd₅Ag₅/C) were investigated in this part. Fig. 5(a) shows the *iR*-corrected HOR polarization curves of the three catalysts collected at 1600 rpm. Pd₉Ag₁/C showed the best HOR activity among these samples, with the largest current density of 0.72 mA cm^{-2} at an overpotential of 100 mV (Fig. 5(b)). This value was obviously higher than that of Pd₅Ag₅/C (0.25 mA cm^{-2} @100 mV) and

Fig. 5. (a) HOR polarization curves in H₂-saturated 0.1 M KOH; (b) Comparison of the current densities and Pd mass activities at an overpotential of 100 mV; (c) Tafel plots of the HOR/HER kinetic currents and corresponding fittings with the Butler-Volmer equation; (d) $j_{0,s}$ and $j_{0,m}$ values for Pd/C, Pd₉Ag₁/C, and Pd₅Ag₅/C; (e) Comparison of the exchange current density ($j_{0,m}$ and $j_{0,s}$) of Pd₉Ag₁/C with those of other reported catalysts; (f) Polarization curves of Pd₉Ag₁/C before and after 1000 CV cycles.

Pd/C (0.27 mA cm⁻² @100 mV). For an accurate comparison, the HOR electrocatalytic activity was normalized by the total Pd mass of the working electrode. As shown in Fig. 5(b), Pd₉Ag₁/C also exhibited the best mass activity for HOR, with a high mass current density of 0.0887 mA mg⁻¹ at a low overpotential of 100 mV. The distinct activities of these samples were ascribed mainly to the different intrinsic activities of the NPs, which was corroborated by their exchange current density (j_0) normalized by the Pd mass or electrochemical surface area (ECSAs) ($j_{0,s}$ or $j_{0,m}$) [32]. The j_0 was calculated using the Butler-Volmer equation (Eq. (1)) [33],

$$j_k = j_0 \left(e^{\frac{\alpha F}{RT} \eta} - e^{-\frac{(\alpha-1)F}{RT} \eta} \right) \quad (1)$$

where α , j_k , j_0 , F , R , T , and η correspond to the transfer coefficient, kinetic current density, exchange current density, Faraday constant (96485 C mol⁻¹), universal gas constant (8.314 J mol⁻¹ K⁻¹), room temperature (298 K), and electron number, respectively.

Typically, j_k is obtained using the Koutecky-Levich equation (Eq. (2)), as shown in Figs. S9(b),(c), S10(b),(c), and S11(b),(c) [34],

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{BC_0\omega^{0.5}} \quad (2)$$

where j_d is the diffusion limited current, B is the Levich constant, C_0 is the hydrogen concentration in 0.1 M KOH, and ω is the rotation speed.

The ECSAs of these samples were calculated based on the ar-

reas of the redox peak of Pd in the cyclic voltammetry (CV) curves, which were obtained in Ar-saturated 0.1 M KOH using a scan rate of 10 mV s⁻¹. The ECSAs of Pd/C, Pd₉Ag₁/C, and Pd₅Ag₅/C were measured to be 22.5, 81.3, and 44.9 m² g⁻¹, respectively (Fig. S12 and Table S1).

As shown in Fig. 5(c),(d), Pd₉Ag₁/C showed the best HOR catalytic activity with the largest $j_{0,s}$ of 0.033 mA cm_{Pd}⁻² and $j_{0,m}$ of 26.5 A g_{Pd}⁻¹. Taking into account the realistic cost and resource of noble metals, $j_{0,m}$ is normally considered more significant than $j_{0,s}$ [32]. The $j_{0,m}$ value of Pd₉Ag₁/C was higher than that of most Pd-based materials, including Pd-CN_x ($j_{0,m}$ = 18.5 A g_{Pd}⁻¹) [35], Pd/C-CeO₂ ($j_{0,m}$ = 24 A g_{Pd}⁻¹) [36], Pd/C-500C ($j_{0,m}$ = 21 A g_{Pd}⁻¹) [37], and Pd/C ($j_{0,m}$ = 22 A g_{Pd}⁻¹) [38] (Fig. 5(e) and Table S2). Additionally, the HOR stability of Pd₉Ag₁/C was further assessed using CV scanning from -0.2 to 1.0 V at 50 mV s⁻¹ in H₂-saturated electrolyte solution (Fig. 5(f)). After the test, the Pd₉Ag₁/C showed negligible degradation, demonstrating the high stability of Pd₉Ag₁/C for HOR in an alkaline medium.

Moreover, the electrocatalytic activity of PdAg/C with a catalyst loading of 1.39 × 10⁻³ g_{cat} cm⁻² on a rotating disk electrode (d = 3 mm) for the HER in an alkaline medium (1.0 M KOH) was also explored. As shown in Fig. 6(a), Pd₉Ag₁/C exhibited the best HER performance among all the catalysts, with the smallest overpotential of 68 mV at a current density of 10 mA cm⁻²; this value was clearly lower than that of Pd/C (η_{10} = 116 mV), Pd₅Ag₅/C (η_{10} = 90 mV), and Pd₁Ag₉/C (η_{10} = 241 mV). The results suggest that the Pd₉Ag₁/C with an optimal ratio of Pd/Ag

Fig. 6. (a) Polarization curves of Pd/C, Pd₉Ag₁/C, Pd₅Ag₅/C, Pd₁Ag₉/C and Ag/C in 1.0 M KOH. (b) Comparison of the overpotential (@10 mA cm⁻²) of Pd₉Ag₁/C and previous Pd-based nanocatalysts. (c) Comparison of the TOF values, mass activity, and Tafel slopes of all the samples; (d) TOF per surface active site and (e) corresponding Tafel plots. (f) Polarization curves of Pd₉Ag₁/C before and after 1000 CV cycles.

displays the highest electrocatalytic activity for the HER. Importantly, the HER activity of Pd₉Ag₁/C was better than that of many recently reported Pd-based electrocatalysts, such as NiCo₂S₄Pd ($\eta_{10} = 83$ mV) [39], PdNi/CNFs ($\eta_{10} = 187$ mV) [40], and solid Pd@Ru ($\eta_{10} = 76$ mV) [41] (Fig. 6(b) and Table S3). To obtain an exact comparison, the electrocatalytic activity of HER was further normalized by the total Pd mass of the working electrode. As shown in Fig. 6(c), Pd₉Ag₁/C also presented the largest mass current density (79.4 A g_{Pd}⁻¹) at an overpotential of 100 mV. To understand the differences in the electrocatalytic activities of the samples in depth, their TOF and Tafel slopes were assessed. As shown in Fig. 6(c),(d), Pd₉Ag₁/C exhibited the largest TOF value of 0.0645 s⁻¹ (at an overpotential of 100 mV); this value was obviously higher than those of the other samples, indicating the excellent intrinsic activity of Pd₉Ag₁/C for the HER. Fig. 6(c), and (e) show the Tafel plots of these samples; Pd₉Ag₁/C showed the lowest Tafel slope of 81.3 mV dec⁻¹, revealing the superior kinetics of Pd₉Ag₁/C for the HER in an alkaline medium. The HER stability of Pd₉Ag₁/C was further evaluated using CV from -0.1 to 0.01 V with a scan rate of 10 mV s⁻¹. As shown in Fig. 6(f), negligible change was observed in the HER activity of Pd₉Ag₁/C before and after 100 CV cycles, indicating the excellent durability of Pd₉Ag₁/C in an alkaline medium.

The excellent catalytic performance of the Pd₉Ag₁/C catalyst for HOR/HER is further discussed. First, the TEM images of the PdAg/C catalyst revealed that small-sized PdAg alloy NPs were well-distributed on the carbon matrix. This was beneficial, as it increased the fraction of metal atoms with an abundance of unsaturated coordination centers and thus the number of accessible active sites for the HOR/HER [10]. Second, although the different alloy samples exhibited similarly sized PdAg NPs,

they were found to have different catalytic activity for the HOR/HER, with Pd₉Ag₁/C being the best electrocatalyst. This vividly demonstrates that the synergistic and alloy effects of PdAg determine the HOR/HER performance of these catalysts. The absolute value of active hydrogen (ΔG^*_{H}) in the HOR/HER is well known to be the key factor for elevating the electrocatalyst. Optimally, ΔG^*_{H} should be around 0; at this value, the surface adsorption of intermediate hydrogen is neither too weak nor too strong. In the literature, the ΔG^*_{H} of metallic Pd has been reported to be less than zero, whereas that of metallic Ag is greater than zero [42], i.e., strong spontaneous hydrogen adsorption occurs on metallic Pd, while the adsorption of hydrogen on metallic Ag is difficult. However, it has been reported that the addition of few of Ag in Pd can induce synergistic and alloy effects that facilitate suitable hydrogen adsorption, and thus enhance the electrocatalytic activity. In the present work, XPS analysis (Figs. S13, 14 and Table S4) revealed that the content of metallic Pd in the three PdAg/C samples were similar, suggesting that the strength of the adsorption of H on Pd was very similar for the three PdAg/C samples, and that the differences in their activities should be ascribed to the different synergistic and alloy effects induced by the amount of metallic Ag. Combined with the electrochemical results, the low content of metallic Ag was found to generate the strongest synergistic and alloy effects for the metallic Pd in Pd₉Ag₁/C to give the most facile adsorption-desorption HER/HOR process, and thus, the best catalytic activity. Increasing the content of metallic Ag led to a decrease in the synergistic and alloy; for this reason, Pd₅Ag₅/C and Pd₁Ag₉/C exhibited inferior HOR/HER activities. These results suggest that the use of a small amount of metallic Ag is critical for maximizing the synergistic and alloy effects, with Pd₁Ag₉/C showing excellent electrocatalytic HOR/HER

activity.

4. Conclusions

In this work, a mortar-pestle milling strategy that did not involve the use of any solvents or organic reagents was developed and used to successfully synthesize a series of PdAg alloy NPs with a small size (4.9 ± 1.03 nm) and good distribution on a carbon matrix. The composition of the alloy NPs was easily tuned by adjusting the atom ratio of the precursors. The size and distribution of the NPs were not obviously influenced by the topological structure of the carbon matrix. The carbon-supported PdAg alloy NPs acted as efficient electrocatalysts for the HOR/HER in an alkaline medium. Pd₉Ag₁/C exhibited the highest activity in the HOR, with the largest $j_{0,m}$ of 26.5 A g_{Pd}⁻¹ and $j_{0,s}$ of 0.033 mA cm_{Pd}⁻², as well as in the HER, with the lowest overpotential of 68 mV at 10 mA cm⁻². The outstanding electrochemical activity was ascribed to the highly distributed small alloy NPs with clean surfaces and thus an abundance of accessible active sites, along with the positive synergistic and alloy effects between the Pd and Ag atoms, which provided excellent intrinsic activity. This study not only provides a scalable, general, and sustainable method to produce supported metal NP catalysts, but also offers a new opportunity to synthesize efficient SMACs for other important reactions.

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Graphical Abstract

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Sustainable solid-state synthesis of uniformly distributed PdAg alloy nanoparticles for electrocatalytic hydrogen oxidation and evolution

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A facile grinding strategy is developed to produce a series of PdAg alloy NPs that are highly dispersed on various carbon supports. The resulting electrocatalysts exhibit excellent activities and stabilities in both the HOR and HER.

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可持续固相合成高分散PdAg合金纳米颗粒用于电催化氢氧化和氢析出反应

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摘要: 固相研磨作为一种新型可持续的合成方法, 近年来引起了人们广泛关注, 为负载型金属合金纳米催化剂的制备提供了新思路。尽管有关合金催化剂研究取得了系列进展, 但现有制备方法大多存在操作步骤复杂、形貌难以控制等问题, 严重制约了合金催化剂的规模化应用。本文发展了一种可持续化策略, 即于室温下在玛瑙研钵中直接研磨合成了一系列高分散在碳载体上的小尺寸PdAg合金纳米颗粒(PdAg/C)。此法无需任何溶剂和有机试剂, 保证了整个过程简单便捷、绿色环保, 同时确保了PdAg合金纳米颗粒表面清洁无污染, 利于样品的催化应用。利用TEM, XRD和XPS表征技术对系列PdAg/C样品的组成及形貌进行了深入探究。TEM结果表明, 所得催化剂中金属颗粒尺寸较小(4.9 ± 1.03 nm), 且高度分散在碳载体表面。XRD结果表明, Pd₉Ag₁/C, Pd₅Ag₅/C和Pd₁Ag₉/C催化剂特征衍射峰位于对应的Pd/C和Ag/C衍射峰之间, 且会随着Ag含量的不断增加逐渐向低角度偏移。XPS结果表明, 三个催化剂中均存在Pd, Ag两种元素, 且随着Ag含量的增加, 它们的Pd 3d结合能逐渐正移; 而随着Pd含量的不断增加, 三样品的Ag 3d结合能逐渐负向偏移。由此可见, 采用可持续固相合成法成功制得了碳负载的PdAg合金纳米颗粒。一系列对比实验表明, PdAg合金纳米颗粒的尺寸和分散度显著依赖于NaOH, 而与碳载体的形貌、比表面积和类型无明显关系。将系列PdAg/C样品用于碱性电催化氢氧化(HOR)和析氢反应(HER)时, 均展现出高的催化性能。其中, Pd₉Ag₁/C催化性能最佳, 在HOR中, 质量交换电流密度和面积交换电流密度分别为26.5 A g_{Pd}⁻¹和0.033 mA cm_{Pd}⁻²; 在HER中, 电流密度为10 mA cm⁻²时所需过电位仅为68 mV; 此外, Pd₉Ag₁/C催化剂经过1000圈CV循环测试后, 催化活性未显著衰减, 对两个目标反应均展现出优异的电化学稳定性。PdAg/C高催化活性主要归因于两个方面: (1) PdAg合金纳米颗粒表面洁净、尺寸小且分散均匀, 能提供大量可利用的活性位点; (2) Pd与Ag之间强的协同与合金效应使得催化剂具有最佳的本征活性。

关键词: 固相合成; 负载型合金纳米颗粒; 电催化; 氢氧化反应; 氢气析出反应

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