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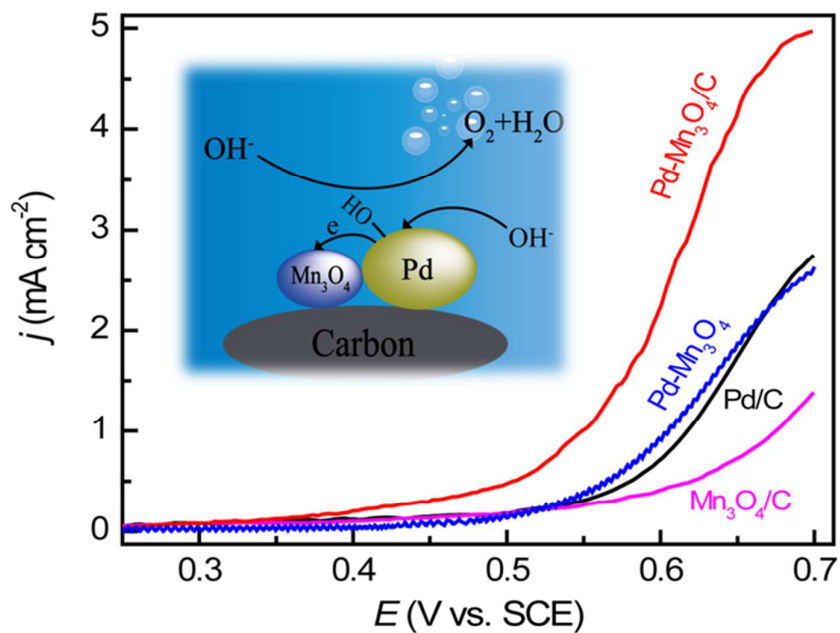


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A high-efficient OER electrocatalyst based on Pd nanoparticles, Mn₃O₄ and carbon black has been designed and exhibited excellent OER activity.

COMMUNICATION

Facile synthesis of Pd-Mn₃O₄/C as High-Efficient Electrocatalyst for Oxygen Evolution Reaction

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Herein, we report the use of carbon black as conducting scaffold to support highly-active Pd and Mn₃O₄ nanoparticles, and demonstrate their enhanced electroactivity for oxygen evolution reaction (OER). Benefiting from the synergistic effect, the as-prepared Pd-Mn₃O₄/carbon black catalyst showed substantially higher OER activity and stability than the Pd-Mn₃O₄ and Pd/C catalysts.

The gas evolution by water electrolysis has attracted more and more attention due to the ever-increasing demand of sustainable and renewable energy sources.¹⁻³ Water electrolysis is generally carried out in alkaline medium because alkaline medium creates possibility for cheap materials to be used as efficient electrodes. If electrical energy is provided by renewable energy sources, such as solar energy, wind energy or tidal energy, the hydrogen production is a carbon free energy carrier, which can be applied to connection with fuel cells to produce energy for a range of applications.⁴ However, the efficiency of water electrolysis in alkaline medium is severely limited by the large anodic overpotential of oxygen evolution reaction (OER).^{5, 6} To address this problem, considerable efforts have been devoted to explore the electrocatalysts with low OER overpotential, and great advances have been achieved.⁶⁻⁸ Noble metals such as Ru, Ir and Pd, *etc.* are widely emerging as the most promising electrocatalysts for OER because of their relatively low overpotential.^{4, 9-14} However, the scarcity and high cost of noble metals severely hinder their applications as electrocatalysts for OER in water electrolysis.

In recent years, numerous efforts have been made to enhance the electrocatalytic activity of noble metal based catalysts and several strategies have been proposed.^{15, 16} Among them, modified noble metals such as Pt-TiO₂, Au-CoO_x and Au-FeO₂ based on the bifunctional mechanism have been indicated one of the most effective method to improve the electrocatalytic activity as well as reduce the cost.¹⁷⁻¹⁹ On the other hand, recent reports have shown that some transition metal oxides such as Mn₃O₄, Co₃O₄, Co-Ni oxide, Ni-Fe oxide have high catalytic activity for OER.²⁰⁻²⁶ Furthermore, supporting the catalysts on conductive and large-surface carbon materials such as carbon nanotubes and graphene has been emerging as one of the most effective method to improve the electrocatalytic activity. For example, Suryanto et al. fabricated

layer-by-layer graphene/cobalt oxide composites as the highly efficient and steady oxygen evolution catalysts compared to the Co₃O₄ catalysts alone.²⁷ Wu et al. synthesized a hybrid consisting of Co₃O₄ nanocrystals supported on single-walled carbon nanotubes and found that Co₃O₄/SWNTs hybrid electrode for the OER exhibits much enhanced catalytic activity as well as superior stability compared with bare Co₃O₄.²⁸ However, to the best of our knowledge, the research on the synergetic effects of noble metals, carbon material and metal oxide towards OER is still rarely reported.^{29, 30}

In this paper, we focused on the development of high performance and low-cost electrocatalyst for OER based on Pd nanoparticles, Mn₃O₄ and carbon black. In comparison to Pt and Au, Pd has substantially higher catalytic activity for OER with lower price.^{9, 14, 31-33} Manganese-based materials have proven to exhibit high activity for OER.³⁴⁻³⁷ However, they suffer from relatively low electrical conductivity. Carbon black is an inexpensive and electrochemically stable conductor commonly used as conductive agent in various electrodes for its low cost, excellent electrical conductivity and good stability. Herein, we report the use of carbon black as conducting scaffold to support highly-active Pd and Mn₃O₄ nanoparticles, and demonstrate their great potential as OER catalyst. Benefiting from the increased surface active oxygen species and surface area as well as improved conductivity, the as-prepared Pd-Mn₃O₄/carbon black (denoted as Pd-Mn₃O₄/C) electrocatalyst showed substantially higher catalytic activity for OER than the Pd-Mn₃O₄ and Pd/C catalysts. The Pd-Mn₃O₄/carbon black catalyst shows a lower onset potential of 63 mV and achieved a remarkably high current density of 5.0 mA cm⁻² at 0.7 V (vs. SCE). Moreover, the Pd-Mn₃O₄/carbon black has excellent long-term stability.

Pd-Mn₃O₄/C electrocatalyst was prepared by a two-step process. Firstly, Mn₃O₄/C powders were synthesized by intermittence microwave irradiation method with a homemade program-controlled microwave oven (1000 W, 2.45 GHz). Transmission electron microscopy (TEM) was performed to study its detailed

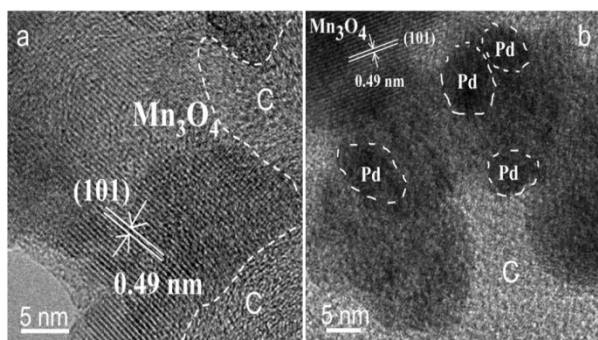


Figure 1. TEM images of (a) $\text{Mn}_3\text{O}_4/\text{C}$ and (b) $\text{Pd-Mn}_3\text{O}_4/\text{C}$.

microstructure. As shown in Figure 1a, Mn_3O_4 has a high crystalline nature, and the parallel fringe with the spacing of 0.49 nm is correspond to the (101) plane of the cubic Mn_3O_4 . The phase of the manganese oxide is characterized as Mn_3O_4 , which is in accordance with the XRD result (Figure S1). Then, Pd nanoparticles was introduced into $\text{Mn}_3\text{O}_4/\text{C}$ by reduction of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution on the $\text{Mn}_3\text{O}_4/\text{C}$ powders using NaBH_4 solution. Figure 1b shows the HRTEM image of the $\text{Pd-Mn}_3\text{O}_4/\text{C}$. The diameters of Pd nanoparticles range from 5 to 10 nm. From the enlarged image (Figure. S2), the parallel fringe with the spacing of 0.22 nm can be clearly observed, which is correspond to the (111) plane of the Pd. The co-existence of parallel fringe with a spacing of 0.22 nm for the (111) plane of the Pd and that with a spacing of 0.49 nm for the (101) plane of the cubic Mn_3O_4 indicates the successful synthesis of $\text{Pd-Mn}_3\text{O}_4/\text{C}$ electrocatalyst.

The chemical bonding states in the $\text{Pd-Mn}_3\text{O}_4/\text{C}$ were further analyzed by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum collected for the $\text{Pd-Mn}_3\text{O}_4/\text{C}$ catalyst is shown in Figure 2a, confirming the existence of Pd, C, O and Mn in the product. The binding energy of C 1s peak locates at 284.8 eV is related to the graphitic carbon for carbon black. The binding energy of Pd 3d is presented in Figure 2b with a $3d_{5/2}$ of 336.2 eV and a $3d_{3/2}$ of 341.6 eV, can be attributed to Pd^0 species.³⁸⁻⁴⁰ All these data show that Pd species attached to the surface of carbon black exist in the form of Pd^0 . In Figure 2c, the XPS spectrum of Mn 2p binding energy shows that the binding energy values of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ are 641.5 eV and 653.4 eV, respectively. The value of Mn $2p_{3/2}$ of 641.5 eV is corresponding to Mn_3O_4 .^{41,42} In addition, it can be

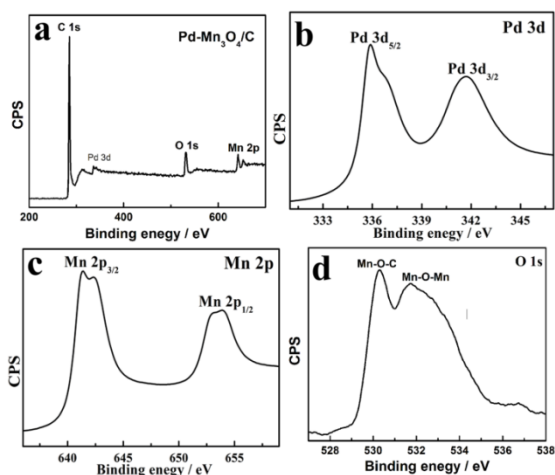


Figure 2. (a) XPS survey, (b) Core level Pd 3d XPS spectrum, (c) Core level Mn 2p XPS spectrum, and Core level O 1s XPS spectrum of the $\text{Pd-Mn}_3\text{O}_4/\text{C}$ catalyst.

observed that there is a spin-orbit splitting of 11.9 eV between the binding energy value of the Mn $2p_{3/2}$ and Mn $2p_{1/2}$, which is in accordance with the spectrum of Mn_3O_4 .⁴¹⁻⁴⁴ This result further indicates that the as-prepared manganese oxide material is Mn_3O_4 . In Figure 2d, the O 1s XPS spectrum of the catalyst shows two different peaks centered at 530.0 and 531.4 eV, which are corresponding to Mn-O-C bond and Mn-O-Mn bond, respectively.⁴⁴

In order to illustrate the advantages of the $\text{Pd-Mn}_3\text{O}_4/\text{C}$ electrocatalyst, the OER activity of Pd/C , $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Pd-Mn}_3\text{O}_4/\text{C}$ is evaluated through linear sweep voltammetric (LSV) curves in 0.1 mol L^{-1} KOH with a sweep rate of 0.001 V s^{-1} . The total loading of catalyst combining Pd and Mn_3O_4 is 0.1 mg cm^{-2} . As shown in

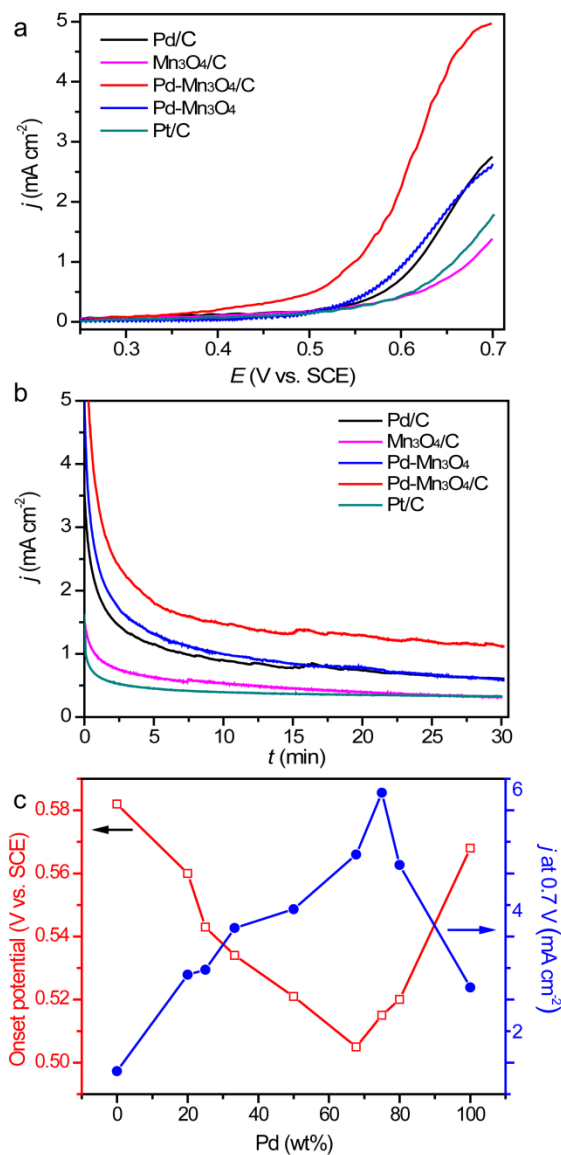


Figure 3. (a) LSV curves with a sweep rate of 0.001 V s^{-1} and (b) Chronoamperometry curves at 0.7 V vs. SCE of Pd/C , $\text{Mn}_3\text{O}_4/\text{C}$, $\text{Pd-Mn}_3\text{O}_4$, $\text{Pd-Mn}_3\text{O}_4/\text{C}$ and Pt/C electrodes in 0.1 mol L^{-1} KOH. (c) Plots of onset potential and the current density at 0.7 V vs. SCE in LSV curves as a function of the Pd weight loading.

Figure 3a, the Pd/C and $\text{Pd-Mn}_3\text{O}_4$ show higher activities than $\text{Mn}_3\text{O}_4/\text{C}$. The onset potential is 0.568 V for the Pd/C and 0.533 for

the Pd-Mn₃O₄, while 0.582 V for the Mn₃O₄/C. The current density at 0.7 V for Pd/C and Pd-Mn₃O₄ is 2.8 and 2.6 mA cm⁻², which is higher than that for the Mn₃O₄/C (1.4 mA cm⁻²). More importantly, in comparison to Mn₃O₄/C, Pd-Mn₃O₄, Pd/C and Pt/C, the Pd-Mn₃O₄/C delivers substantially higher electrocatalytic activity, showing that the synergistic effect of Mn₃O₄ and C can greatly improve the electrocatalytic activity of Pd. The onset potential of Pd-Mn₃O₄/C shifts negatively to 0.505V, which is significantly smaller than those of the Mn₃O₄/C, Pd-Mn₃O₄ and Pd/C. Additionally, it should be noted that the Pd mass loading in this Pd-Mn₃O₄/C catalyst is only 0.066 mg cm⁻², much smaller than the Pd/C catalyst (Pd mass loading: 0.1 mg cm⁻²). Moreover, the Pd-Mn₃O₄/C catalyst has an excellent stability for OER. As shown in Figure 3b, the Pd-Mn₃O₄/C catalyst exhibited a slower current decay over time than the Mn₃O₄/C, Pd-Mn₃O₄ and Pd/C. In addition, the Pd-Mn₃O₄/C catalyst showed much higher current densities than the Mn₃O₄/C, Pd-Mn₃O₄ and Pd/C, indicating that the Pd-Mn₃O₄/C catalyst has the best electroactive for OER. All these results fully support our assumption that supporting highly-active Pd on Mn₃O₄ and carbon black not only can significantly improve its electrocatalytic activity as well as stability, but also could obviously decrease the Pd loading without sacrifice of its activity.

To study the effect of the Pd mass on the electrocatalytic activity, Pd-Mn₃O₄/C catalysts with various ratios have been synthesized by similar method. Figure 3c compares the onset potential and the current density at 0.7 V of LSV curves for the Pd-Mn₃O₄/C catalysts with different weight percent of Pd. The total loading of catalyst combining by Pd and Mn₃O₄ is 0.1 mg cm⁻² for the Pd-Mn₃O₄/C electrode. The lowest onset potential of 0.505 V was achieved when the weight ratio for Pd to Mn₃O₄ is 2:1. This value is 63 mV lower than that for the Pd/C. The current density at 0.7 V of the Pd-Mn₃O₄/C is 5.0 mA cm⁻², which is 1.8 times higher than that of Pd/C and 1.3 times. More importantly, the enhanced performance is more remarkable than that of CoO_x/Pd,¹⁸ NiO/Pd,⁴⁵ and even more obvious than that of recent reported Co₃O₄/Au (the onset potential is 30 mV lower than that for Co₃O₄).⁴⁶ In addition, it can be seen that the current density at 0.7 V increases with the increase Pd content but decreases again when it reaches a maximum value as the weight percent of Pd is 75% or weight ratio is 1: 3 for Mn₃O₄ to Pd. All these results indicate that Pd-Mn₃O₄/C catalysts with Pd to Mn₃O₄ weight ratio of 2:1 to 3:1 have the best performance.

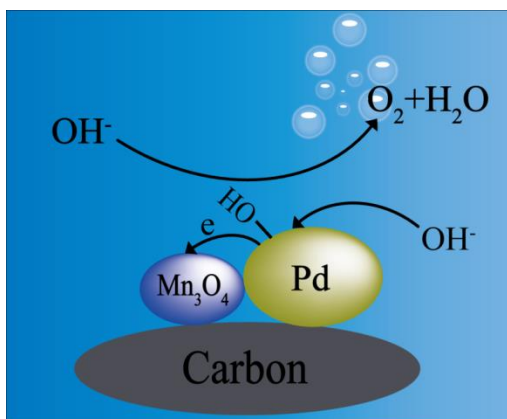
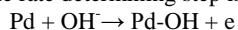


Figure 4. Mechanism for OER on the Pd-Mn₃O₄/C. The schematic presentation of the plausible pathway of the OER.

Although the real understanding of the mechanism for OER on the Pd-Mn₃O₄/C electrocatalyst is still undergoing, a general understanding is that the rate determining step is as following:



It means the efficient of OER is determined by the bound energy of Pd-OH and the Pd-OH is the active center of OER.⁴⁷⁻⁵⁰ For further understanding the intrinsic reaction of enhanced OER performance on the Pd-Mn₃O₄/C catalyst, the XPS data of pure Pd/C, Mn₃O₄/C and Pd-Mn₃O₄/C catalysts were compared in Figure S2. The XPS data show that the peak of Pd 3d of Pd-Mn₃O₄/C (335.8 eV) is slightly higher-shifted than that of pure Pd/C (335.6 eV), which indicates that the Pd of Pd-Mn₃O₄/C is more electron poor. Meanwhile, the peak of Mn 2p of Pd-Mn₃O₄/C (641.1 eV) is slightly lower-shifted than that of pure Mn₃O₄/C (641.3 eV). It is suggested that electron may donate from Pd to Mn₃O₄ and modify the electronic structure of Pd, which enhances the electro-activity of Pd. The presence of strong electrophilic Pd will accelerate to form the Pd-OH via nucleophilic reaction with OH⁻ (Figure 4). This kind of synergistic effect between Pd and Mn₃O₄ is particularly important to improve the OER property of Pd-Mn₃O₄/C.

Conclusions

In summary, highly active Pd-Mn₃O₄/C composite Mn₃O₄ has been successfully developed and demonstrated as an excellent catalyst for efficient OER in alkaline solution. The Pd-Mn₃O₄/C catalyst obtained by the intermittent microwave heating method and chemical reduction exhibits substantially enhanced OER activity compared to the Mn₃O₄/C, Pd-Mn₃O₄ and Pd/C catalyst. The Pd-Mn₃O₄/C catalyst shows a low onset potential of 63 mV and achieved a remarkably high current density of 5.0 mA cm⁻² at 0.7 V (vs. SCE), which are superior or comparable to the recently reported noble metal based catalysts. Such the outstanding electrocatalytic activity is attributed to the synergetic effects of Pd, Mn₃O₄ and C that enables the composite has enhanced conductivity for charge transport and more active sites as well as surface area for OER reaction. This work provides new insights into using transition metal oxide and carbon materials as high performance electrocatalyst for OER in water electrolysis.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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