



Electron-rich platinum electrocatalysts supported onto tin oxides for efficient oxygen reduction

Guojie Chao^a, Xingyu An^a, Longsheng Zhang^b, Jing Tian^a, Wei Fan^{a,*}, Tianxi Liu^{a,b}

^a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials College of Materials Science and Engineering, College of Mechanical Engineering, Donghua University, Shanghai, 201620, PR China

^b Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, International Joint Research Laboratory for Nano Energy Composites, Jiangnan University, Wuxi, 214122, PR China

ARTICLE INFO

Keywords:

Electrocatalyst
Oxygen reduction reaction
Platinum
Electron density

ABSTRACT

Developing high-performance electrocatalysts for the oxygen reduction reaction (ORR) is of significance for metal-air batteries and fuel cells. The platinum (Pt) catalyst is considered as the most ideal candidate for its highest catalytic activity towards ORR. However, the practical application of Pt catalyst is impeded for its high cost and poor catalytic stability. Here, we seek to use the SnO₂ support to modify the electronic structures of Pt catalyst to boost its catalytic activity and durability. We synthesized Pt/SnO₂ heterojunction catalyst with Pt nanoparticles anchored on SnO₂ supports, which has the similar morphology to commercial Pt/C with Pt nanoparticles anchored on carbon supports. By means of X-ray photoelectron spectroscopy, we find that the electron density of the Pt nanoparticles supported on SnO₂ is increased, while no such features are found in the Pt/C catalyst. Comparing with the Pt/C catalyst, the Pt/SnO₂ catalyst exhibits higher activity and better durability for ORR catalysis, which can be ascribed to the strong metal-support interactions between Pt nanoparticles and SnO₂ supports.

1. Introduction

The electrochemical oxygen reduction reaction (ORR) is crucial for the development of various energy systems and technologies, like metal-air batteries and fuel cells [1–5]. To date, platinum (Pt) catalysts possess the highest ORR activities, but their potentials have not yet fully unfolded [6–8]. Further advancements in enhancing the intrinsic activities and catalytic stabilities of Pt-based ORR catalysts are desired to meet the requirements of practical applications.

Recently, semiconducting metal oxides (e. g. TiO₂, SnO₂, WO₃ and ZrO₂, etc.) were reported as promising catalyst supports for various electrochemical reactions [9–15]. Strong metal-support interactions were found in such heterojunction electrocatalysts, which could modify the electronic structures of metal active sites and enhance their intrinsic activities [16–24]. As a typical semiconducting metal oxide, tin oxide (SnO₂) has great potential due to its nontoxicity, low cost and superior electrochemical stability. As reported, the SnO₂ has shown great potential to function as support for boosting the catalytic activity and stability of electrocatalyst [10,25,26]. Moreover, it was found that the SnO₂ could also facilitate the desorption of oxygen-containing

intermediates during the ORR process [12]. We posit that designing Pt/SnO₂ hybrid catalysts with nanostructured Pt and SnO₂ support can induce strong interactions between them and modify the electronic structures of Pt, thus obtaining enhanced ORR performance.

Here, we report a facile approach to prepare Pt/SnO₂ heterojunction catalysts with Pt nanoparticles anchored onto SnO₂ supports. Using X-ray photoelectron spectroscopy (XPS), we have found that the SnO₂ supports can induce electron-rich features of Pt nanoparticles in Pt/SnO₂ catalyst, which are found to be beneficial for enhancing the intrinsic activities of Pt active sites towards ORR catalysis. In sharp contrast, no such features are found in commercial Pt/C catalyst with Pt nanoparticles anchored onto carbon supports. Comparing with the commercial Pt/C, the Pt/SnO₂ exhibits higher half-wave potential and lower Tafel slope, verifying its superior ORR performance. Besides, the Pt/SnO₂ catalyst shows greatly improved catalytic durability compared with the Pt/C catalyst. These results, taken together, indicate the significant role of metal-support interactions for enhancing the ORR performance of Pt catalyst.

* Corresponding author.

E-mail address: weifan@dhu.edu.cn (W. Fan).

<https://doi.org/10.1016/j.coco.2020.100603>

Received 7 November 2020; Received in revised form 16 December 2020; Accepted 16 December 2020

Available online 2 February 2021

2452-2139/© 2021 Elsevier Ltd. All rights reserved.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP) (M.W. 10000), Tin (IV) chloride (SnCl_4) and commercial Pt/C (20 wt%) were got from Sigma-Aldrich. The oleylamine (technical grade, 80%), oleic acid (technical grade, 90%), cyclohexane and ethanol were brought from Energy Chemical. Ethylene glycol (98%) and chloroplatinic acid (99%) were brought from MACK-LIN. All chemicals were used without further purification.

2.2. Preparation of Pt/SnO₂ hybrid catalysts

First, SnO₂ supports were prepared via a hydrothermal method [27]. Typically, SnCl₄ (199 μL) were added into a mixed solvent of oleylamine (2.5 mL) and oleic acid (20 mL) under stirring, followed by the addition of ethanol (10 mL). The mixture solution was kept at 160 °C for 6 h in one Teflon-lined autoclave. After centrifugation and washing for 5 times, the precipitates were collected and dried in vacuum for 5 h to obtain SnO₂ supports. The PVP and chloroplatinic acid were separately dissolved in ethylene glycol by using the phial under ultrasonic treatment. Afterwards, the as-obtained SnO₂ powders (40 mg) were added into ethylene glycol (30 mL) under stirring and the mixture was kept at 160 °C, followed by drop-by-drop addition of PVP solution (10 mg/mL, 3 mL) and chloroplatinic acid solution (80 mg/mL, 3 mL). After 1 h treating, the resulting precipitate was collected by centrifugation and washed by using ethyl alcohol. Finally, the Pt/SnO₂ hybrid catalyst was obtained after drying the precipitates at 50 °C in vacuum for 5 h.

2.3. Electrochemical measurements

An electrochemical workstation (CHI-760D) was used to perform the

electrochemical tests. The Ag/AgCl electrode is employed as the reference electrode and the graphite rod was used as the counter electrode. Cyclic voltammetry (CV) curves and Linear sweep voltammetry (LSV) curves were recorded with a three-electrode system by using the rotating ring disk electrode (RRDE) technique.

3. Results and discussion

The SnO₂ supports were first synthesized through a hydrothermal method, followed by a solvothermal process to prepare Pt/SnO₂ hybrids. As shown in the transmission electron microscopy (TEM) image of the synthesized Pt/SnO₂ sample (Fig. 1a), the Pt nanoparticles are uniformly attached on the SnO₂ supports and the diameters of Pt nanoparticles are about 4–7 nm. In the TEM image of Pt/SnO₂, it is clearly seen the characteristic lattice spacing of the (111) crystal plane of Pt and the (110) crystal plane of SnO₂ (Fig. 1b). As displayed in Fig. 1c, the TEM and corresponding energy dispersive spectroscopy images of Pt/SnO₂ reveal a homogeneous distribution of Pt, Sn and O elements. Large contact areas are formed between the Pt nanoparticles and SnO₂ supports to induce strong metal-support interactions.

The powder X-ray diffraction (XRD) was employed to analyze the compositions of obtained samples. As shown in the XRD pattern, the diffraction peaks of SnO₂ sample can be indexed to SnO₂ (PDF No. 41-1445) in tetragonal phase (Fig. S1). We further compare the structures of the synthesized Pt/SnO₂ catalyst and commercial Pt/C, with respect to the effect of catalyst supports. Upon comparison of the XRD patterns of the above two samples (Fig. 2a), it can be seen that their characteristic peaks are similar, indicating the same crystal form of Pt in both samples. No diffraction peaks of impurity are found in the XRD pattern of the prepared Pt/SnO₂. In the TEM image of the Pt/C catalyst (Fig. S2), it is clearly observed that the Pt nanoparticles are anchored on carbon supports with uniform diameters in the range of 3–5 nm. The Pt/

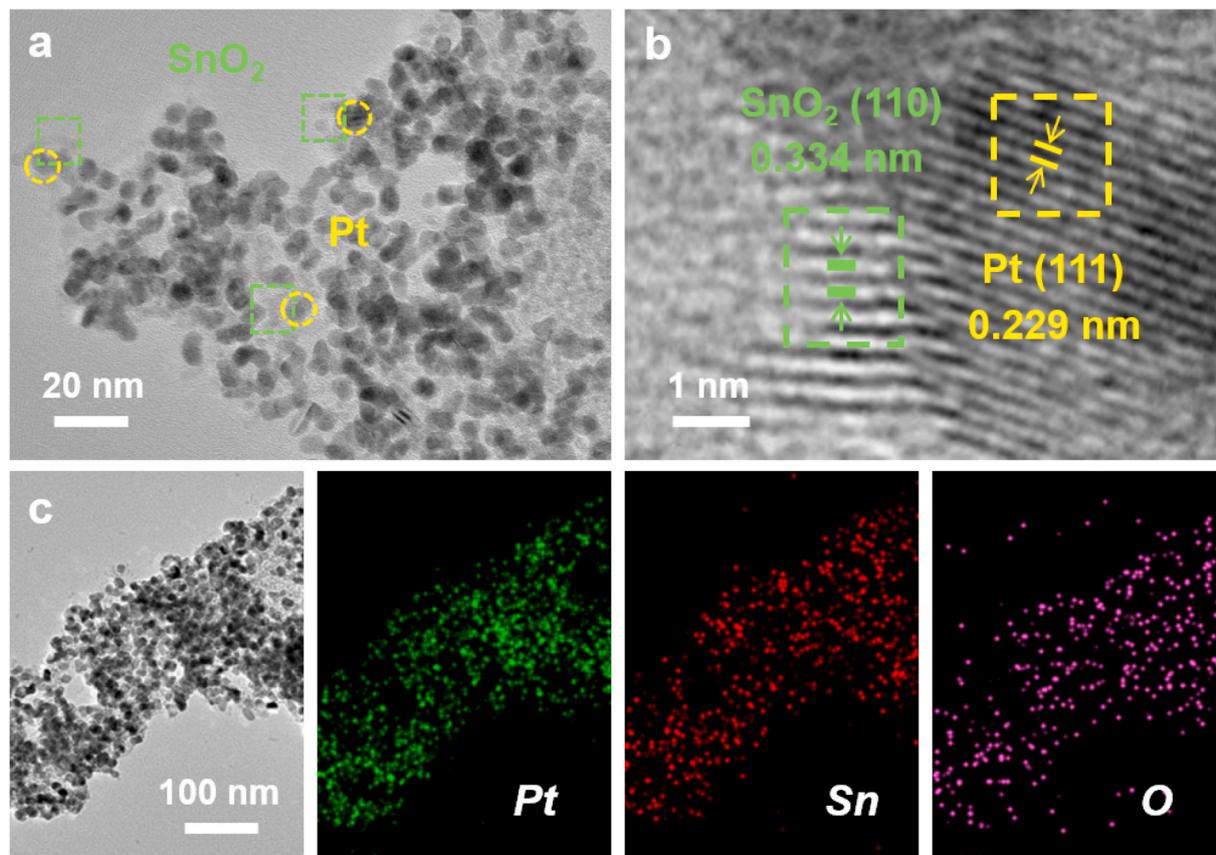


Fig. 1. (a, b) TEM images of Pt/SnO₂ sample. (c) TEM and corresponding elemental mapping images of Pt/SnO₂ sample.

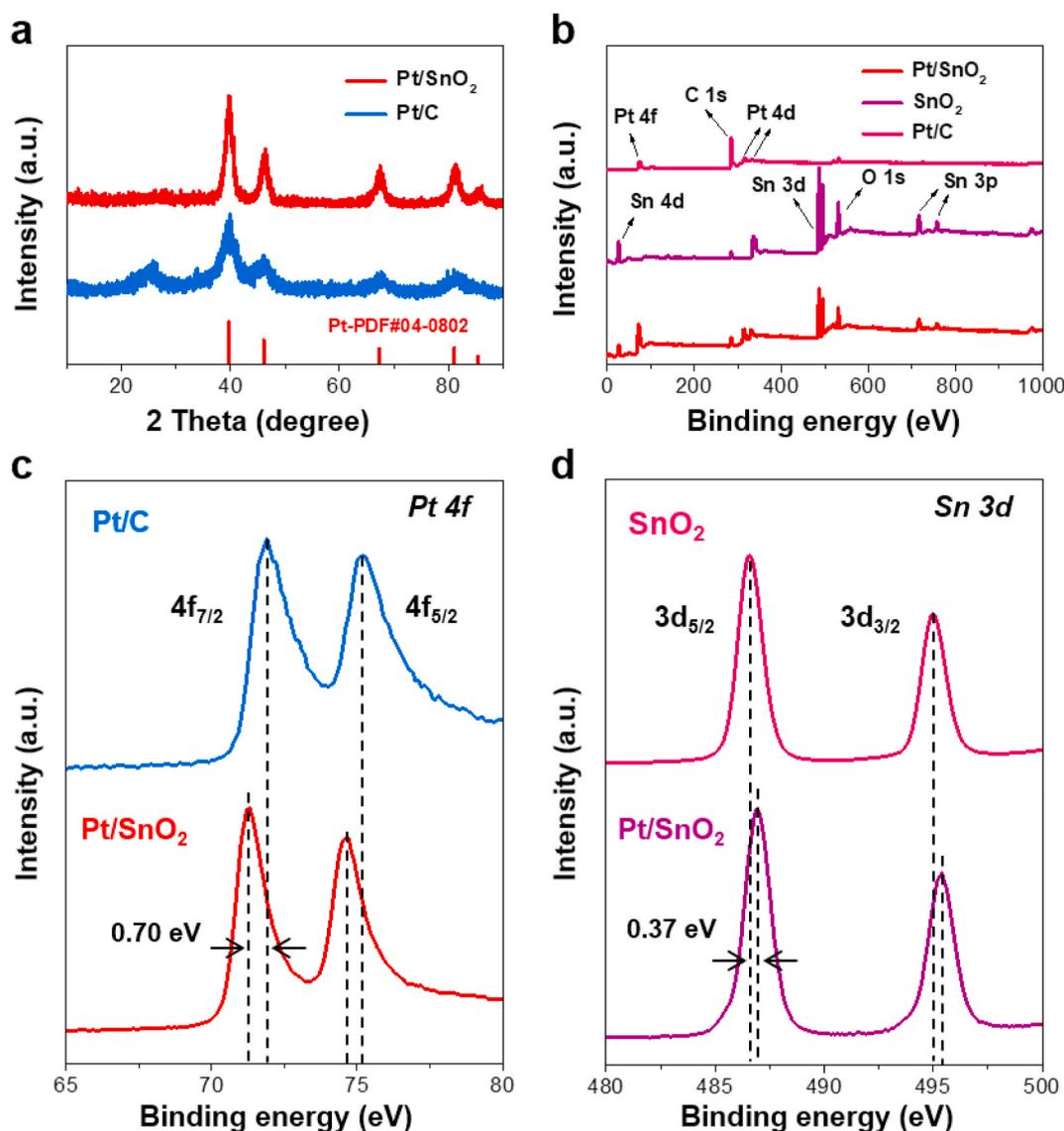


Fig. 2. (a) XRD patterns of Pt/SnO₂ and Pt/C samples. (b) XPS spectra of SnO₂, Pt/C and Pt/SnO₂ samples. (c) High-resolution Pt 4f spectra of Pt/C and Pt/SnO₂ samples. (d) High-resolution Sn 3d spectra of SnO₂ and Pt/SnO₂ samples.

C catalyst shows similar morphology and crystal structure to the obtained Pt/SnO₂ catalyst.

The chemical state of elements in the Pt/C and Pt/SnO₂ samples were further assessed by XPS measurements. As shown in Fig. 2b, the signals of Pt elements are observed in the XPS spectra of these catalysts, while the characteristic peaks of Sn elements are only seen in the corresponding spectrum of Pt/SnO₂ catalyst. In the high-resolution Pt 4f spectra of catalysts (Fig. 2c), two prominent peaks can be respectively indexed to Pt 4f_{7/2} and Pt 4f_{5/2} peaks. Notably, the Pt 4f_{7/2} and Pt 4f_{5/2} peaks of the Pt nanoparticles in Pt/SnO₂ catalyst show ~0.70 eV downshift compared with those of the commercial Pt/C, suggesting that the Pt nanoparticles supported on SnO₂ have higher electron density than those on carbon supports. As reported, the metal-support interactions between SnO₂ supports and Pt nanoparticles can tune the electronic structures of Pt [14,28]. It is possibly that the electrons transfer from the SnO₂ supports to Pt nanoparticles at the heterojunction interfaces, thereby increasing the electron density of Pt nanoparticles supported on SnO₂. Accordingly, the Sn 3d_{5/2} and Sn 3d_{3/2} peaks and the O1s peak of SnO₂ of Pt/SnO₂ catalyst all exhibit positive shifts compared with those of Pt/C catalyst (Fig. 2d and Fig. S3), which verifies the electron transfers from the SnO₂ supports to Pt nanoparticles in the

Pt/SnO₂ catalyst.

To evaluate the effect of SnO₂ and carbon supports towards ORR catalysis, we further carried out the electrochemical measurements of the Pt/SnO₂ and Pt/C catalysts. As shown in Fig. 3a and Fig. S4, additional reduction peaks can be seen in the CV curves of these two catalysts measured in the O₂-saturated electrolytes compared with the CV curves in N₂-saturated electrolytes, indicating the existence of ORR process. Notably, the reduction peak in the CV curves of Pt/SnO₂ catalyst is more positive than that of commercial Pt/C catalyst, which indicates the Pt/SnO₂ has higher ORR activity. We further carried out the LSV tests of these catalysts using RRDE technique (Fig. 3b). The LSV curve of Pt/SnO₂ catalyst shows an improved half-wave potential (0.862 V vs. reversible hydrogen electrode, RHE), higher than that of Pt/C (0.851 vs. RHE), indicating the superior ORR activity of Pt/SnO₂ catalyst. Notably, the pure SnO₂ support shows poor catalytic activity toward ORR (Fig. S5). The increased catalytic activity of Pt/SnO₂ catalyst is attributed to the enhancement of intrinsic activity of Pt nanoparticles anchored on the SnO₂ support. Moreover, comparing with Pt/C catalyst, the Pt/SnO₂ catalyst has smaller Tafel slope (Fig. 3c), which suggests its increased reaction kinetics towards ORR catalysis.

We further calculated the electron-transfer number and peroxide

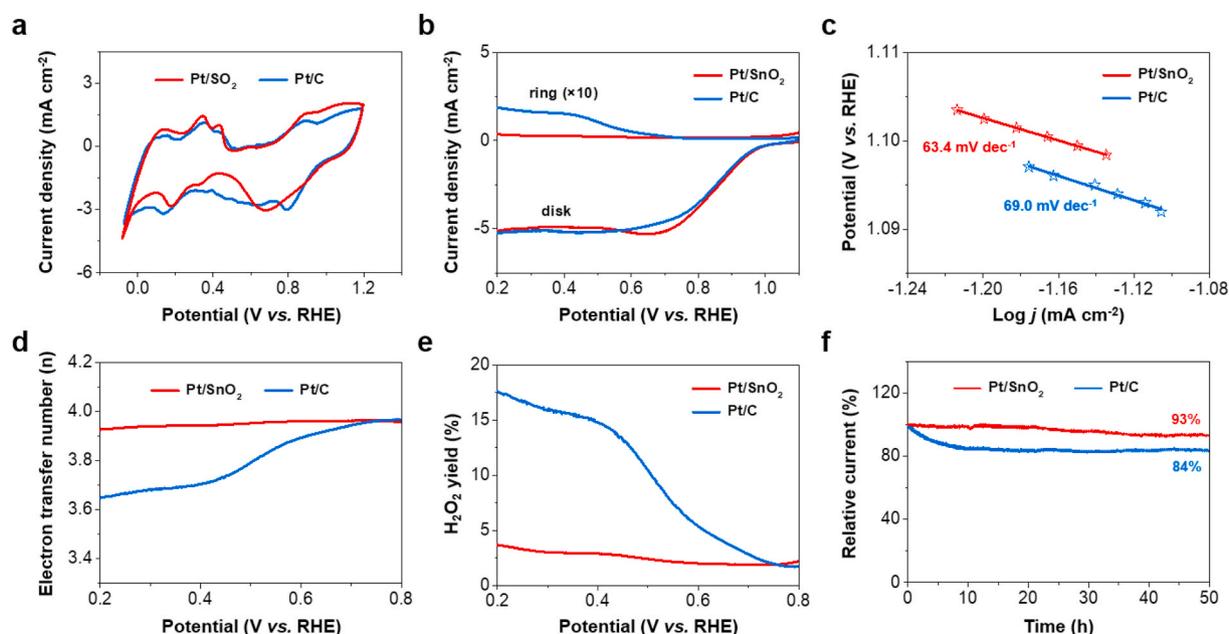


Fig. 3. (a, b) CV and LSV curves of Pt/SnO₂ and Pt/C catalysts, respectively. (c–e) Tafel curves, electron transfer number and H₂O₂ yield of Pt/SnO₂ and Pt/C catalysts, respectively. (f) Normalized *i*-*t* curves of Pt/SnO₂ and Pt/C catalysts.

(H₂O₂) yield of Pt/SnO₂ and Pt/C catalysts from their RRDE polarization curves. The electron transfer number of Pt/SnO₂ catalyst is much closer to 4 than that of Pt/C catalyst during the ORR process (Fig. 3d). Besides, comparing with Pt/C catalyst, the Pt/SnO₂ catalyst owns a lower H₂O₂ yield, which illustrate the prepared Pt/SnO₂ catalyst has better ORR performance (Fig. 3e). In conjunction with XPS analysis and electrochemical results, it is reasonable to conclude that the improved ORR activity of Pt/SnO₂ catalyst is attributed to the electron-rich features of Pt catalytic sites in Pt/SnO₂ catalyst. The current versus time (*i*-*t*) chronoamperometric test was performed to study the durability of catalysts. As shown in Fig. 3f, the Pt/SnO₂ has a good current retention (93%) after 50 h of continuous operation, while the Pt/C catalyst suffers fast current decay (17%) during the test.

4. Conclusion

In summary, we report one facile strategy to prepare Pt/SnO₂ heterojunction catalyst with Pt nanoparticles uniformly anchored onto SnO₂ supports. The generated strong metal-support interactions between Pt and SnO₂ can modify the electronic structures of Pt sites. Using XPS studies, we have verified that the SnO₂ supports can increase the electron densities in Pt nanoparticles of the Pt/SnO₂ catalyst while no such features are found in Pt/C catalyst. Comparing with Pt/C catalyst, the Pt/SnO₂ catalyst exhibit superior catalytic activity and durability towards ORR, indicating the significant role of metal-support interactions in the Pt/SnO₂ catalyst. In a broader context, this work provides a general principle to structure heterogeneous catalysts with optimal supports in various electrochemical reactions.

CRediT authorship contribution statement

Guojie Chao: Investigation, Methodology, Data processing, Writing-original draft. **Xingyu An:** Investigation. **Longsheng Zhang:** Conceptualization, Writing-review & editing. **Jing Tian:** Writing-review & editing, Visualization. **Wei Fan:** Funding acquisition, Writing-review & editing, Supervision. **Tianxi Liu:** Funding acquisition, Writing-review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors are grateful for the financial support from the Fundamental Research Funds for the Central Universities (2232019A3-03), the National Natural Science Foundation of China (21704014), Shanghai Scientific and Technological Innovation Project (18JC1410600), Shanghai Municipal Education Commission (17CG33).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.coco.2020.100603>.

References

- [1] B.C.H. Steele, A. Heinzel, Materials for fuel-cell technologies, *Nature* 414 (2001) 345–352.
- [2] M. Li, Z. Zhao, T. Cheng, A. Fortunelli, C.Y. Chen, R. Yu, Q. Zhang, L. Gu, B. V. Merinov, Z. Lin, E. Zhu, T. Yu, Q. Jia, J. Guo, L. Zhang, W.A. Goddard, Y. Huang, X. Duan, Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction, *Science* 354 (2016) 1414–1419.
- [3] J. Wang, Z. Huang, W. Liu, C. Chang, H. Tang, Z. Li, W. Chen, C. Jia, T. Yao, S. Wei, Y. Wu, Y. Lie, Design of N-coordinated dual-metal sites: a stable and active Pt-free catalyst for acidic oxygen reduction reaction, *J. Am. Chem. Soc.* 139 (2017) 17281–17284.
- [4] T. Zhu, Q. Feng, S. Liu, C. Zhang, Metallogel-derived 3D porous carbon nanosheet composites as an electrocatalyst for oxygen reduction reaction, *Compos. Commun.* 20 (2020) 100376.
- [5] G.J. Chao, L.S. Zhang, D. Wang, S. Chen, H.L. Guo, K.B. Xu, W. Fan, T.X. Liu, Activation of graphitic nitrogen sites for boosting oxygen reduction, *Carbon* 159 (2020) 611–616.
- [6] Y. Yuan, J. Wang, S. Adimi, H. Shen, T. Thomas, R. Ma, J.P. Attfield, M. Yang, Zirconium nitride catalysts surpass platinum for oxygen reduction, *Nat. Mater.* 19 (2020) 282–286.
- [7] X. Wang, M.T. Swihart, G. Wu, Achievements, challenges and perspectives on cathode catalysts in proton exchange membrane fuel cells for transportation, *Nat. Catal.* 2 (2019) 578–589.
- [8] M. Qiao, Y. Wang, Q. Wang, G. Hu, X. Mamat, S. Zhang, S. Wang, Hierarchically ordered porous carbon with atomically dispersed Fe₂N₄ for ultraefficient oxygen

- reduction reaction in proton-exchange membrane fuel cells, *Angew. Chem. Int. Ed.* 59 (2020) 2688–2694.
- [9] C. Gebauer, D. Hoffmann, Z. Jusys, R.J. Behm, Novel, Highly conductive Pt/TiO₂ thin-film model catalyst electrodes: the role of metal-support interactions, *Chemelectrochem* 3 (2016) 1553–1563.
- [10] G. Cognard, G. Ozouf, C. Beauger, G. Berthome, D. Riassetto, L. Dubau, R. Chattot, M. Chatenet, F. Maillard, Benefits and limitations of Pt nanoparticles supported on highly porous antimony-doped tin dioxide aerogel as alternative cathode material for proton-exchange membrane fuel cells, *Appl. Catal., B* 201 (2017) 381–390.
- [11] F.L. Lai, W. Zong, G.J. He, Y. Xu, H.W. Huang, B. Weng, D.W. Rao, J.A. Martens, J. Hofkens, I.P. Parkin, T.X. Liu, N₂ Electroreduction to NH₃ by selenium vacancy-rich ReSe₂ catalysis at an abrupt interface, *Angew. Chem. Int. Ed.* 59 (2020) 13320–13327.
- [12] X. Shen, T. Nagai, F. Yang, L. Zhou, Y. Pan, L. Yao, D. Wu, Y. Liu, J. Feng, J. Guo, H. Jia, Z. Peng, Dual-site cascade oxygen reduction mechanism on SnO₂/Pt-Cu-Ni for promoting reaction kinetics, *J. Am. Chem. Soc.* 141 (2019) 9463–9467.
- [13] H. Chhina, S. Campbell, O. Kesler, Ex situ evaluation of tungsten oxide as a catalyst support for PEMFCs, *J. Electrochem. Soc.* 154 (2007) B533–B539.
- [14] F.B. Ometto, E.A. Carbonio, E. Teixeira-Neto, H.M. Villullas, Changes induced by transition metal oxides in Pt nanoparticles unveil the effects of electronic properties on oxygen reduction activity, *J. Mater. Chem.* 7 (2019) 2075–2086.
- [15] L.S. Zhang, L.P. Wang, Y.Z. Wen, F.L. Ni, B. Zhang, H.S. Peng, Boosting neutral water oxidation through surface oxygen modulation, *Adv. Mater.* 32 (2020) 2002297.
- [16] S.J. Tauster, S.C. Fung, R.T. Baker, J.A. Horsley, Strong interactions in supported-metal catalysts, *Science* 211 (1981) 1121–1125.
- [17] A. Lewera, L. Timperman, A. Roguska, N. Alonso-Vante, Metal-support interactions between nanosized Pt and metal oxides (WO₃ and TiO₂) studied using X-ray photoelectron spectroscopy, *J. Phys. Chem. C* 115 (2011) 20153–20159.
- [18] B.R. Camacho, C. Morais, M.A. Valenzuela, N. Alonso-Vante, Enhancing oxygen reduction reaction activity and stability of platinum via oxide-carbon composites, *Catal. Today* 202 (2013) 36–43.
- [19] J. Ftouni, A. Munoz-Murillo, A. Goryachev, J.P. Hofmann, E.J.M. Hensen, L. Lu, C. J. Kiely, P.C.A. Bruijninx, B.M. Weckhuysen, ZrO₂ Is Preferred over TiO₂ as support for the Ru-catalyzed hydrogenation of levulinic acid to gamma-valerolactone, *ACS Catal.* 6 (2016) 5462–5472.
- [20] J.H. Kim, S. Chang, Y.T. Kim, Compressive strain as the main origin of enhanced oxygen reduction reaction activity for Pt electrocatalysts on chromium-doped titania support, *Appl. Catal. B Environ.* 158 (2014) 112–118.
- [21] L.S. Zhang, L.P. Wang, H.P. Lin, Y.X. Liu, J.Y. Ye, Y.Z. Wen, A. Chen, L. Wang, F. L. Ni, Z.Y. Zhou, S.G. Sun, Y.Y. Li, B. Zhang, H.S. Peng, A lattice-oxygen-involved reaction pathway to boost urea oxidation, *Angew. Chem. Int. Ed.* 58 (2019) 16820–16825.
- [22] A.G.M. da Silva, C.G. Fernandes, Z.D. Hood, R. Peng, Z.L. Wu, A.H.B. Dourado, L. S. Parreira, D.C. de Oliveira, P.H.C. Camargo, S.I.C. de Torresi, PdPt-TiO₂ nanowires: correlating composition, electronic effects and O-vacancies with activities towards water splitting and oxygen reduction, *Appl. Catal., B* 277 (2020) 119177.
- [23] I. Jimenez-Morales, F. Haidar, S. Cavaliere, D. Jones, J. Roziere, Strong interaction between platinum nanoparticles and tantalum-doped tin oxide nanofibers and its activation and stabilization effects for oxygen reduction reaction, *ACS Catal.* 10 (2020) 10399–10411.
- [24] K.M. Naik, E. Higuchi, H. Inoue, Two-dimensional oxygen-deficient TiO₂ nanosheets-supported Pt nanoparticles as durable catalyst for oxygen reduction reaction in proton exchange membrane fuel cells, *J. Power Sources* 455 (2020) 227972.
- [25] Y. Yang, X.A. Yang, D. Leng, S.B. Wang, W.B. Zhang, Fabrication of g-C₃N₄/SnS₂/SnO₂ nanocomposites for promoting photocatalytic reduction of aqueous Cr(VI) under visible light, *Chem. Eng. J.* 335 (2018) 491–500.
- [26] P. Zhang, S.Y. Huang, B.N. Popov, Mesoporous tin oxide as an oxidation-resistant catalyst support for proton exchange membrane fuel cells, *J. Electrochem. Soc.* 157 (2010) B1163–B1172.
- [27] S. Liu, J. Xiao, X. Lu, J. Wang, X. Wang, X.W. Lou, Efficient electrochemical reduction of CO₂ to HCOOH over sub-2nm SnO₂ quantum wires with exposed grain boundaries, *Angew. Chem. Int. Ed.* 58 (2019) 8499–8503.
- [28] S. Hussain, N. Kongi, H. Erikson, M. Rahn, M. Merisalu, L. Matisen, P. Paiste, J. Aruvali, V. Sammelselg, L.A. Estudillo-Wong, K. Tammeveski, N. Alonso-Vante, Platinum nanoparticles photo-deposited on SnO₂-C composites: an active and durable electrocatalyst for the oxygen reduction reaction, *Electrochim. Acta* 316 (2019) 162–172.