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Janus Structured Pt-FeNC Nanoparticles as Catalyst for the Oxygen Reduction Reaction

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We present a new Janus structured catalyst consisting of Pt nanoparticles on Fe-N-C nanoparticles encapsulated by graphene layers for ORR. The ORR activity of the catalyst increases under potential cycling as the unique Janus nanostructure is further bonded due to the synergetic effect. The present study describes an important advanced approach for the future design of efficient, stable, and low-cost Pt-based electrocatalytic systems.

The main approaches to enhance the performance of Pt electrocatalyst toward oxygen reduction reaction (ORR) are to control the particle size and improve the surface structure by alloying it with other metal.¹⁻⁴ Towards this goal, various morphologies of Pt-M (metal) catalyst viz. core-shell, ordered intermetallic have been studied.⁵⁻⁸ These structures have shown remarkable enhancement in the ORR activity but their durability still remains questionable. A new approach to mitigate this would be the synthesis of Janus structures that has a unique ability to increase the durability of the catalyst. Janus nanostructures are a class of hetero-nanostructures that specifically comprise two materials that are bonded adjacently into a single particle. The combination of the two materials in these nanostructures can be tailored specifically to give rise to a synergistic effect, resulting in a substantial increase in their desired efficacy. Although colloidal metal-semiconductor Janus nanostructures are particularly attractive as photoactive materials,⁹⁻¹¹ they have not been used as an electrocatalyst particularly because semiconductors lack the hydrogenation activity of OH_{ad} on its surface to produce water.

There has been great progress in the development of Fe-N-C embedded on graphene as non-precious catalyst for ORR, particularly the ones pyrolyzed at high temperature as their performance has been demonstrated to be promising for PEMFC applications.^{12, 13} However their catalytic activity rate compared to the carbon supported Pt catalysts is still

insufficient.¹⁴ Herein we report on an electrodeposited Janus structure comprising Pt-FeN_xC_y (denoted as Pt-FeNC) nanoparticles encapsulated by graphene layers. Detailed synthesis of FeN_xC_y moieties on graphene is described in the supporting information. Fe demetallation from the FeN_xC_y catalysts was done by acid washing in order to eliminate the inactive Fe species. Pulse deposition was applied to deposit the Pt nanoparticles on the FeN_xC_y particles. The Pt clusters nucleate on FeN_xC_y particles and exhibit a higher mass activity than the commercial Pt/C catalyst for the ORR. This new methodology of electrodeposited Janus structures is very promising to increase the ORR activity and durability of the catalyst.

Figure 1 a-c show the high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images of Janus structured Pt-FeNC. The average particle size observed for FeN_xC_y particles is 16 nm whereas the average Pt cluster

Fig.1 (a) HAADF-STEM image of Pt-FeNC nanoparticles encapsulated in graphene. (b) HAADF-STEM image of a single Pt-FeNC nanoparticle along with its EDS spectra showing Fe (yellow) and both Pt, Fe (red) peaks.(c) Magnified image from a different particle showing the Janus structure along with its (d) EDS (blue for the larger particle and red for the smaller one).

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Fig.2 (a, b) XANES and FT-EXAFS analysis of Fe-N-C catalyst respectively. .

size is 2.0 nm. Magnified STEM images from a single particle (Figure 1b, c) clearly show the Janus structure comprising Pt nanoparticles nucleated on FeN_xC_y particle. EDS analysis (Figure 1d) from Figure 1c indicates that the smaller particle is Pt (red) and the larger Fe particle (blue) contains no traces of PtFe alloy. Even though bulk PtFe alloy is not detected, the direct contact between the Pt and FeN_xC_y particles should lead to the formation of a bond, leading to enhanced stability as discussed below. HAADF-STEM images also show that some of the Pt nanoparticles are independent (not attached to FeN_xC_y nanoparticles). The apparent reason being as potential pulses are applied during the deposition, Pt cluster nucleation and Janus structure formation on FeN_xC_y nanoparticles occurs discretely. This two-step process of Pt cluster nucleation and Janus structure formation continues and finally the last pulse that nucleates the Pt cluster stays independent due to the lack of sufficient energy for diffusion toward FeN_xC_y nanoparticles. Although the structures of high temperature treated Fe-N-C catalysts have been extensively studied, no consensus has been reached to its origins for high stability.^{12, 15, 16} Fe porphyrins (5 wt. %) embedded in graphene pyrolyzed in NH_3 at 700°C produces Fe-N-C nanoparticles. To evaluate the structure of FeN_xC_y catalyst we undertook synchrotron X-ray absorption spectroscopy (XAS) analysis and compared it to the literature.^{17, 18} Figure 2a shows the X-ray absorption near-edge structure (XANES) at the Fe K-edge, indicating the absence of pre-edge in the FeN_xC_y catalyst compared to Fe foil and

revealing a broken D_{4h} symmetry.¹⁹ A comprehensive quantitative analysis of the Fourier transform (FT) X-ray absorption fine structure (EXAFS) is beyond the scope of this manuscript. However, earlier detailed studies using EXAFS and Mössbauer spectroscopy have clearly shown that 97% of the Fe exists as mononuclear iron centers in FeN_xC_y moieties.¹⁷ A qualitative analysis shows identical FT-EXAFS peaks for our Fe-N-C catalyst system, indicating almost no Fe crystalline structures and the existence of FeN_xC_y moieties. Recent DFT studies have also discussed the formation of FeN_xC_y moieties on graphene sheets.^{20, 21}

Figure 3a depicts cyclic voltammograms (CV) of Janus structured Pt-FeNC and commercial Pt/C (TKK, 46.6 wt. %) in 0.1 M HClO_4 acid with a scan rate of 20 mV s^{-1} . Due to the graphene layers and very low loading of Pt in the Janus structured Pt-FeNC catalyst, 2.1 $\mu\text{g cm}^{-2}$ as determined by ICP-MS, no prominent H adsorption peaks at the potential range between 0.1 and 0.4 V were observed. The as-synthesized Pt-FeNC catalyst at 0.9V exhibits a high initial Pt mass activity for ORR (0.69 A mg^{-1}), which is about 3 times higher than the commercial Pt/C catalyst (0.22 A mg^{-1}). Stability of Pt has been a major concern for the ORR electrocatalyst, so we evaluated durability by an accelerated test involving potential cycling between 0.6V and 1.0V versus RHE with a scan rate of 50 mV s^{-1} in an air-saturated HClO_4 solution. Figure 3b compares the mass activity of the Pt-FeNC and Pt/C catalysts after 10,000 potential cycles. Compared to the Pt/C catalyst, the Janus structured Pt-FeNC catalyst showed a reverse trend. Potential

Fig.3 (a) CV of graphene encapsulated Pt-FeNC and commercial Pt/C recorded in Ar-saturated 0.1 M HClO_4 solution at room temperature. (b) Comparison of mass activities at 0.9 V for Pt-FeNC and commercial Pt/C catalyst.

Fig.4 (a, b) CV and ORR curves for the graphene encapsulated Pt-FeNC nanoparticles with a scan rate of 20 mV s^{-1} and 10 mV s^{-1} respectively in 0.1 M HClO_4 acid. (c) HAADF-STEM image of Pt-FeNC nanoparticles after 25,000 potential cycle test. (d) Magnified image from a single particle after cycling test showing the Janus structure along with its (e) EDS (blue for the larger particle and red for the smaller one).

cycling has been known to cause agglomeration, Oswald ripening and dissolution of the commercial Pt/C catalyst, resulting in a reduction in its ORR activity.²²⁻²⁴ A reduction of 12 mV in half wave potential for the Pt/C catalyst indicated a 19% decrease in mass activity after just 10,000 potential cycles (Fig.S2b). On the other hand, potential cycling increased the half wave potential for the Janus structured Pt-FeNC catalyst, thus boosting its Pt mass activity to 0.75 A mg^{-1} after 10,000 cycles (Figure 3b). To elucidate that the ORR activity for the Pt-FeNC catalyst does not decrease, further potential cycles were employed. The cycling causes an unnoticeable increase in the H adsorption/ desorption region as shown in Figure 4a but a very large positive shift in the half wave potential (Figure 4b). The changes in half wave potential and Pt mass activity after potential cycles are compiled in Table S1. After 25,000 cycles, the Pt mass activity increased to 0.85 A mg^{-1} , behaving in an opposite trend to that of the Pt/C catalyst. To evaluate the opposite trend, TEM diagnosis was done for the sample after 25,000 cycles. No agglomeration or Oswald ripening was observed from the HAADF-STEM image as shown in figure 4c. Further in-depth analysis of a single particle from the same sample indicates that the Pt-FeNC Janus structure is intact (Figure 4d and Figure S1). EDS analysis shown in figure 4e from the particle indicates a further interaction of Pt with FeNC nanoparticles. Independent Pt nanoparticles observed initially (Figure 1a, b) were incorporated with FeNC nanoparticles during the potential cycling, thereby forming randomly dispersed Pt nanoparticles embedded in a single FeNC nanoparticle (Figure S1d). We envisage that the increase in synergy between the Pt nanoparticles and FeNC nanoparticles

changes the electronic structure of Pt and thus enhances the overall ORR activity of the Janus structured Pt-FeNC catalyst.²⁵ In summary, this communication presents a new strategy to improve the activity and stability of the ORR by tuning the Janus structure of the catalyst comprising Pt nanoparticles electrodeposited on Fe-N-C nanoparticles. The Janus structure plays a bifunctional role of tuning the electronic structure of Pt nanoparticles due to the synergetic effect and simultaneously increases the durability of the catalyst by further bonding at the interface between the Pt and the Fe-N-C nanoparticles. The present study enlightens an important advanced approach for the future design of efficient, stable, and low-cost Pt-based electrocatalytic systems.

Notes and references

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1. V. R. Stamenkovic, B. S. Mun, K. J. J. Mayrhofer, P. N. Ross and N. M. Markovic, *J Am Chem Soc*, 2006, **128**, 8813-8819.
2. C. Chen, Y. J. Kang, Z. Y. Huo, Z. W. Zhu, W. Y. Huang, H. L. L. Xin, J. D. Snyder, D. G. Li, J. A. Herron, M. Mavrikakis, M. F. Chi, K. L. More, Y. D. Li, N. M. Markovic, G. A. Somorjai, P. D. Yang and V. R. Stamenkovic, *Science*, 2014, **343**, 1339-1343.
3. E. Antolini, *Appl Catal B-Environ*, 2016, **181**, 298-313.
4. Y. C. Qin, X. Zhang, X. P. Dai, H. Sun, Y. Yang, X. S. Li, Q. X. Shi, D. W. Gao, H. Wang, N. F. Yu and S. G. Sun, *Small*, 2016, **12**, 524-533.
5. G. W. Wang, B. Huang, L. Xiao, Z. D. Ren, H. Chen, D. L. Wang, H. D. Abruna, J. T. Lu and L. Zhuang, *J Am Chem Soc*, 2014, **136**, 9643-9649.
6. K. A. Kuttiyiel, Y. Choi, S. M. Hwang, G. G. Park, T. H. Yang, D. Su, K. Sasaki, P. Liu and R. R. Adzic, *Nano Energy*, 2015, **13**, 442-449.
7. Y. M. Choi, K. A. Kuttiyiel, J. P. Labis, K. Sasaki, G. G. Park, T. H. Yang and R. R. Adzic, *Top Catal*, 2013, **56**, 1059-1064.
8. D. L. Wang, H. L. L. Xin, R. Hovden, H. S. Wang, Y. C. Yu, D. A. Muller, F. J. DiSalvo and H. D. Abruna, *Nat Mater*, 2013, **12**, 81-87.
9. A. Vaneski, A. S. Sussha, J. Rodriguez-Fernandez, M. Berr, F. Jackel, J. Feldmann and A. L. Rogach, *Adv Funct Mater*, 2011, **21**, 1547-1556.
10. U. Banin, Y. Ben-Shahar and K. Vinokurov, *Chem Mater*, 2014, **26**, 97-110.
11. S. Liang, X. L. Liu, Y. Z. Yang, Y. L. Wang, J. H. Wang, Z. J. Yang, L. B. Wang, S. F. Jia, X. F. Yu, L. Zhou, J. B. Wang, J. Zeng, Q. Q. Wang and Z. Y. Zhang, *Nano Lett*, 2012, **12**, 5281-5286.
12. E. Proietti, F. Jaouen, M. Lefevre, N. Larouche, J. Tian, J. Herranz and J. P. Dodelet, *Nat Commun*, 2011, **2**.
13. Y. Y. Jiang, Y. Z. Lu, X. Y. Lv, D. X. Han, Q. X. Zhang, L. Niu and W. Chen, *Acs Catal*, 2013, **3**, 1263-1271.
14. Y. Liu, X. Yue, K. Li, J. Qiao, D. Wilkinson and J. Zhang, *Journal of Coordination Chemistry Reviews*, 2016, **315**, 153.
15. M. Lefevre, E. Proietti, F. Jaouen and J. P. Dodelet, *Science*, 2009, **324**, 71-74.
16. Z. W. Chen, D. Higgins, A. P. Yu, L. Zhang and J. J. Zhang, *Energ Environ Sci*, 2011, **4**, 3167-3192.
17. C. H. Choi, C. Baldizzone, G. Polymeros, E. Pizzutillo, O. Kasian, A. K. Schuppert, N. R. Sahraie, M. T. Sougrati, K. J. J. Mayrhofer and F. Jaouen, *Acs Catal*, 2016, **6**, 3136-3146.
18. A. Zitolo, V. Goellner, V. Armel, M. T. Sougrati, T. Mineva, L. Stievano, E. Fonda and F. Jaouen, *Nat Mater*, 2015, **14**, 937-+.
19. N. Ramaswamy, U. Tylus, Q. Y. Jia and S. Mukerjee, *J Am Chem Soc*, 2013, **135**, 15443-15449.
20. C. E. Szakacs, M. Lefevre, U. I. Kramm, J. P. Dodelet and F. Vidal, *Phys Chem Chem Phys*, 2014, **16**, 13654-13661.
21. E. F. Holby, G. Wu, P. Zelenay and C. D. Taylor, *J Phys Chem C*, 2014, **118**, 14388-14393.
22. Z. H. Hou, M. W. Li, M. J. Han, J. H. Zeng and S. J. Liao, *Electrochim Acta*, 2014, **134**, 187-192.
23. J. Zeng, J. Y. Lee, J. Chen, P. K. Shen and S. Song, *Fuel Cells*, 2007, **7**, 285-290.
24. M. K. Debe, A. K. Schmoeckel, G. D. Vernstrorn and R. Atanasoski, *J Power Sources*, 2006, **161**, 1002-1011.
25. X. P. Han, F. Y. Cheng, T. R. Zhang, J. G. Yang, Y. X. Hu and J. Chen, *Adv Mater*, 2014, **26**, 2047-2051.