Defective Graphene Anchored Iron-Cobalt Nanoparticles for Efficient Electrocatalytic Oxygen Reduction†

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Xuecheng Yan,^a Yi Jia,^a Longzhou Zhang,^a Mun Teng Soo^b and Xiangdong Yao^{*a}

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A kind of non-precious FeCo nanoparticles decorated defective graphene (DG) sample DG@FeCo was successfully synthesized via a facile impregnation method. It is shown that the DG@FeCo exhibits similar oxygen reduction reaction activity to that of the commercial Pt/C, but with much better durability and free from methanol poisoning in alkaline electrolytes.

The efficient use of renewable and clean energy is the ultimate goal for the sustainable development of human beings. Of which, fuel cell is receiving increasing research attention in recent years due to its high energy efficiency and the diversity of the fuel supply. Particularly clean energy, such as hydrogen and alcohols can be used to power fuel cells.^{1,2} Unfortunately, the sluggish cathodic oxygen reduction reaction (ORR) of fuel cells considerably hinders their overall capability. At present, extensive effort has been devoting to explore alternatives to replace the current expensive yet unstable ORR catalyst platinum (Pt). The most widely investigated materials are transition metals due to their remarkable ORR activity as well as their high abundance in the earth, typical examples including iron (Fe) and cobalt (Co).³⁻⁵

Recent studies show that carbon materials with certain types of defects not only could serve as highly efficient metal-free ORR catalysts,⁶⁻⁹ but also promising materials to anchor, disperse and interact with metal particles,¹⁰⁻¹² boosting the ORR performance of the resultant catalysts, particularly in alkaline media. In our previous work,⁹ it was revealed that a kind of defective graphene (DG) could effectively catalyze the electrochemical reactions, such as the ORR. Both the experimental results and the theoretical calculations confirmed that certain types of defects, such as the combination of pentagon, heptagon and octagon (pentagon-octagon-pentagon (5-8-5), heptagon-pentagon-pentagon-heptagon (7-5-5-7), etc.), could act

as the active sites for the electrochemical reactions. In view of the carbon material is essential to the electrocatalysts, and FeCo alloy could effectively catalyze the ORR.¹³⁻¹⁵ In this work, we used the highly active defective graphene as a host for the FeCo nanoparticles, aiming to combine the merits of these two materials and fabricate non-precious metal based electrocatalysts with greatly enhanced ORR performance, and accompanied by an economical cost as well. For comparison, single Fe and Co loaded DG samples were also synthesized, showing the influence of metals on the ORR. Meanwhile, FeCo nanoparticles decorated pristine graphene was also fabricated to verify the effect of defects towards the ORR. The experimental results show that the DG anchored FeCo sample DG@FeCo demonstrates the highest ORR activity among the synthesized catalysts. Remarkably, the ORR performance of the DG@FeCo is similar to that of the commercial Pt/C (20 wt% Pt), especially the half-wave potential (0.816 V vs. 0.815 V, vs. RHE). Moreover, the DG@FeCo is much more stable than the Pt/C and free from methanol poisoning, indicating that it is a promising catalyst to be used in methanol-powered fuel cells.

The synthesized sample DG@FeCo was firstly characterized by transmission electron microscopy (TEM). It can be seen from Fig. 1a that the metal particles are homogeneously dispersed on the defective graphene. The insert histogram in Fig. 1a shows that the majority of the loaded metals are around 10 nm in diameter. The X-ray powder diffraction (XRD) pattern of the DG@FeCo in Fig. 1b reveals that the dominant phase of the loaded metals is FeCo alloy, which matches well with the standard XRD pattern (JCPDS Card No. 65-6829). The peak centered at 26.3° is from the graphitic carbon,^{16,17} as shown in Fig. 1b by comparing the XRD pattern of the reference sample defective graphene. We can also observe weak diffraction peaks of iron oxide in the XRD pattern of DG@FeCo, most likely due to the surface oxidation of Fe. Interestingly, no detectable Co peak was found in the XRD pattern of DG@FeCo, implying that all of the Co has been alloyed with Fe. The corresponding energy-dispersive X-ray spectroscopy (EDS) elemental-mapping images of the DG@FeCo in Fig. 1(c-g) show the distributions of C, O, Fe and Co, which further verify Fe and Co are presented in the form of FeCo alloy in DG@FeCo, since the mapping images of Fe and

^aSchool of Natural Sciences and Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan Campus, QLD 4111, Australia.
E-mail: x.yao@griffith.edu.au

^bMaterials Engineering, The University of Queensland, St. Lucia, QLD 4072, Australia.

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Fig. 1 (a) TEM image of the prepared sample DG@FeCo (Inset: a histogram shows the metal particle size distribution); (b) XRD patterns of the prepared sample DG@FeCo and DG; (c)-(g) EDS elemental mapping images of the DG@FeCo showing the distribution of carbon, oxygen, iron and cobalt; (h) The corresponding SAED pattern of the sample DG@FeCo.

Co in Fig. 1f and g are matched very well in the relevant areas. Besides, the existence of oxygen in the DG@FeCo may come from the oxygen-containing functional groups in the defective graphene or the trace metal oxide, consistent with the X-ray photoelectron spectroscopy (XPS) results of the DG sample (Fig. S1, ESI†). The corresponding selected area electron diffraction (SAED) pattern in Fig. 1h further confirms that Fe and Co are presented in the form of FeCo alloy in DG@FeCo. Specifically, the calculated lattice spaces from the diffraction rings are 2.02, 1.43 and 1.16 Å, respectively, which agrees well with the lattice spaces of FeCo alloy (110), (200) and (211) planes in Fig. 1b. The XPS survey spectra in Fig. S2 (ESI†) reveal the surface states of the Fe and Co in the sample DG@FeCo, showing that the metal surface is partially oxidized due to the unstable nature of metallic FeCo alloy.

Besides the FeCo alloy nanoparticles, the samples composed of single metal Fe/Co and defective graphene were also prepared for comparison, denoted as DG@Fe and DG@Co, respectively. From the XRD pattern in Fig. S3 (ESI†), it can be seen that the major phase is metallic Fe, and a small percentage of oxidized Fe (Fe_3O_4) was also detected in the DG@Fe sample. However, nearly all the Co is existed in metallic state, as indicated by the XRD pattern of DG@Co in Fig. S4 (ESI†). It is worth mentioning that the particle sizes of single Fe and Co are much bigger than that of the FeCo alloy on the defective graphene (Fig. S5 and S6, ESI†), for example, the particle size of Fe in DG@Fe is not uniform, ranging from 5 nm to nearly 100 nm, and most of them are around 15 nm (Fig.

S5, ESI†). Meanwhile, the single Co loaded DG sample DG@Co shows even bigger particle size than that of the DG@Fe. As can be seen from Fig. S6 (ESI†), the Co particles show very wide size distribution, from 10 nm to 220 nm, and the majority of them are centered at 50 nm. The small particle size as well as the uniform distribution of the FeCo alloy in the DG@FeCo sample may render it highly active for electrocatalytic reactions.

The ORR performance of the prepared samples as well as the commercial Pt/C (20 wt% Pt) was evaluated in an O_2 -saturated 0.1 M KOH solution by a rotating disk electrode (RDE). As can be seen from the corresponding ORR polarization curves in Fig. 2a, the FeCo alloy loaded defective graphene sample DG@FeCo shows the highest ORR activity among the resultant catalysts, in terms of half-wave potential ($E_{1/2}$), onset potential (E_{onset}) and limiting current density as well. The super ORR activity of the DG@FeCo can be observed more clearly from the $E_{1/2}$ and E_{onset} comparisons in Fig. 2b. Impressively, the DG@FeCo is as good as the commercial Pt/C to catalyze the ORR (Fig. 2a and 2b). In particular, its $E_{1/2}$ is similar to that of the Pt/C (0.816 V vs. 0.815 V, vs. RHE). In the meantime, the DG@Fe also exhibits improved ORR performance, especially the current density is increased obviously compared to the DG. However, the sample DG@Co shows negligible $E_{1/2}$ increase, possibly due to the introduced Co particles are too big to catalyze the ORR. In addition, to elucidate the excellent ORR performance of the DG@FeCo is not mainly inherited from the FeCo nanoparticles, in this work, we synthesized a pure FeCo alloy sample denoted as FeCo, the corresponding XRD pattern can be found in Fig. S7 (ESI†). It is observed from Fig. S8 (ESI†) that the pure FeCo sample shows very low ORR activity. Apparently, the high ORR activity of DG@FeCo is derived from the FeCo alloy phase, and may also

Fig. 2 (a) Polarization curves of the prepared samples and Pt/C measured at the rotation speed of 1600 rpm in an O_2 -saturated 0.1 M KOH solution; (b) Half-wave potential and onset potential comparisons of the synthesized samples; (c) Polarization curves at different rotation speeds of the DG@FeCo; (d) Tafel plots of the DG@FeCo and the commercial Pt/C.

benefited from the uniform as well as the small metal particles of the FeCo alloy. In addition, the influence of Pt, if any, from the Pt counter electrode on the ORR activity of DG@FeCo can be excluded, as the testing results are almost the same by using a graphite rod as the counter electrode (Fig. S9, ESI†). Furthermore, in order to study the influence of the carbon component of the catalyst on the ORR, a sample denoted as G@FeCo was prepared by using the pristine graphene (G) combined with the FeCo nanoparticles. The XRD pattern shows that FeCo was also presented in the form of FeCo alloy in G@FeCo (Fig. S10, ESI†), and most of the metal particles are around 11 nm (Fig. S11, ESI†), which is slightly bigger than that of the DG@FeCo (Fig. 1a, insert). The ORR test results in Fig. S12 (ESI†) reveal that the G@FeCo sample is much less active than that of the defective graphene anchored FeCo sample DG@FeCo, further confirming the crucial role of carbon defects in prompting the ORR, as reported in our previous investigations.⁶⁻¹⁰ It provides another evidence to show that the impressive ORR performance of the DG@FeCo sample is derived from the synergic effects between the carbon defects in the DG and the introduced FeCo nanoparticles. Herein, the unique defects in the DG could anchor more FeCo grain during the initial stage of the catalyst preparation. Since the designed metal content is the same for DG@FeCo and G@FeCo, it is reasonable that the metal particle size in the DG is smaller than that of in the G. Another reason is that the defects on graphene are enriched with dangling bonds¹⁸ that could achieve stronger interactions with the FeCo nanoparticles,^{19,20} which can also be beneficial for improving the catalytic activity and durability of the resultant catalyst.

Given that the DG@FeCo shows the highest ORR activity among the resultant samples, more detailed test was carried out on this catalyst to reveal the reaction mechanism. Fig. 2c presents the polarization curves of the DG@FeCo scanned from 400 to 2500 rpm. It is obvious that the current density shows a linear relationship with the rotation speed, indicating the ORR is a well-defined kinetics controlled process. The corresponding Koutecky–Levich (K–L) plots of DG@FeCo under different potentials show good linearity (Fig. S13, ESI†), certifying that the dissolution of oxygen during the ORR process belongs to the first-order reaction kinetics.^{5,21} In addition, the excellent reaction kinetics of the DG@FeCo for the ORR was also revealed by a small Tafel slope of 39 mV per decade at low overpotentials, while this value is 46 mV per decade for the Pt/C (Fig. 2d), indicating our catalyst DG@FeCo could reach the steady current faster than the Pt/C. Furthermore, the high ORR efficiency of the DG@FeCo can also be gleaned from the low percentage of peroxide species and nearly four electron transfer number (around 3.8), as calculated from the rotating ring-disk electrode (RRDE) data (Fig. S14, ESI†). For example, the peroxide species yield is less than 8 % for the DG@FeCo in the potential range of 0.2 to 0.7 V (vs. RHE), which is in the same level as the Pt/C. The exceptional ORR performance as well as the low cost of the DG@FeCo may render it as a potential catalyst to substitute the commercial Pt/C for practical fuel cell and metal-air battery applications.

It is apparent that the combination of the unique carbon defects in the defective graphene and the introduced small and uniform FeCo nanoparticles facilitate the ORR of the DG@FeCo. As it was revealed by our previous studies, the unique defects in the carbon materials could act as the ORR

active sites,⁶⁻¹⁰ and the loaded FeCo nanoparticles could provide additional reaction sites for the oxygen.¹⁴⁻¹⁶ The synergistic coupling effects between the carbon defects and the FeCo nanoparticle is possible to form an advantageous local coordination environment, which could reduce the reaction barrier as well as the charge-transfer resistance during the ORR process,^{10,14} thus the DG@FeCo sample shows outstanding ORR activity in alkaline media, which is comparable to that of the commercial Pt/C. Besides, it is suggested that smaller metal particles are more favorable than the bigger counterparts for the ORR, since the chemical bonding between metal particles and defects on the DG becomes stronger and charge transfer may occur,²² which will be benefit for the electrocatalytic reactions, such as for the ORR. In order to verify our assumptions, the electrochemical active surface areas (ECSAs) of the prepared samples DG@FeCo and G@FeCo were tested in the 0.1 M KOH solution, followed by the reported method.²³ The results show that the ECSA of the DG@FeCo is 151 cm², which is higher than that of the G@FeCo (128 cm²), as indicated in Fig. S15 (ESI†), further proving that the DG is a more favorable material to anchor, disperse as well as interact with metal particles than normal carbon materials to catalyze the electrochemical reactions. Since the metallic FeCo is not stable under the electrochemical test conditions, to probe the real active sites of the DG@FeCo, we conducted the XPS and XRD measurement for DG@FeCo after the ORR test. It can be observed from Fig. S16 (ESI†) that the surface Fe and Co in the DG@FeCo sample after the ORR evaluation are presented in the form of iron oxide and cobalt oxide, respectively. Since the ORR happens on the surface of the catalysts, it is therefore reasonable to deduce that the metal oxides are crucial to the ORR. However, the bulk is still metallic FeCo alloy after the

Fig. 3 (a) Amperometric *i*-*t* curves of the DG@FeCo and the Pt/C tested at 1000 rpm in an O₂-saturated 0.1 M KOH solution; (b) ORR polarization curves of the DG@FeCo measured before and after 5000 potential cycles at a scan rate of 10 mV s⁻¹ with the rotation speed of 1600 rpm in an O₂-saturated 0.1 M KOH solution; (c) and (d) Methanol tolerance test with 5% methanol (in volume) in an O₂-saturated 0.1 M KOH solution for the DG@FeCo and the commercial Pt/C.

ORR assessment, as shown in the XRD pattern (Fig. S17, ESI†). Herein, it is apparent that the surface metal oxides are important to the ORR, but the bulk metallic FeCo alloy is also essential, since it could enhance the electron transfer efficiency during the ORR process because of its high conductivity, which is consist with the previous studies.²⁴⁻²⁶

Apart from the activity, the durability of the ORR catalysts is another crucial factor for their practical applications. In this work, we evaluated the stability of the DG@FeCo by different methods, for comparison, the commercial Pt/C was also assessed under the same conditions. From the amperometric $i-t$ test results in Fig. 3a, it is clear that the DG@FeCo is much more stable than the Pt/C for the ORR in an alkaline solution. For instance, after continuous test in an O₂-saturated 0.1 M KOH electrolyte for 20 000 s, the DG@FeCo could maintain 97.0% of its initial current, while the Pt/C only retained 80.6% of the starting current, showing that the DG@FeCo is much more stable than the Pt/C under the amperometric $i-t$ test conditions. Besides, the accelerated durability test was also applied to evaluate the DG@FeCo and the Pt/C in alkaline electrolytes. From Fig. 3b, we can see that after cyclic voltammetry (CV) cycling for 5 000 cycles, the half-wave potential of the DG@FeCo was only negatively shifted 10 mV; however, the commercial Pt/C exhibits a more serious attenuation of 17 mV under the same test conditions (Fig. S18, ESI†). Both durability test results prove that our catalyst DG@FeCo is more stable than the Pt/C towards the ORR in alkaline media, most likely due to the strong interactions between the FeCo nanoparticles and the carbon defects in DG. It is known that methanol as a kind of clean energy source can be used in a variety of fields, a case in point is to power fuel cells.²⁷ In this regard, the cathodic ORR catalysts should have the capability to withstand the methanol cross-over effect if methanol is used as the fuel. For the methanol tolerance test, we introduced 5% (in volume) methanol into an O₂-saturated 0.1 M KOH medium and stirred it for 5 min to make it mix homogeneously with the electrolyte. The CV measurement was conducted before and after adding methanol. It can be observed from Fig. 3c that the DG@FeCo was not affected by the introduction of methanol, since the ORR peak almost kept unchanged. Nevertheless, the commercial Pt/C nearly lost its ORR catalytic activity after the addition of methanol, as evidenced by the vanishing of the ORR peak and the appearing of the strong methanol oxidation peak (Fig. 3d). It means that the DG@FeCo catalyst is also a promising candidate to catalyze the ORR in methanol based fuel cells.

In conclusion, a facile impregnation method was successfully utilized to prepare a highly active ORR catalyst with an economical production cost. It is shown that the resulting sample DG@FeCo exhibits extraordinary ORR performance in alkaline media. Besides, the DG@FeCo sample is more stable than the Pt/C and free from methanol poisoning. Our study demonstrates that the unique carbon defects play key roles in promoting the ORR, such as assisting the formation of small and uniform FeCo nanoparticles on the DG, and interacting strongly with the nanoparticles. Overall, this

research opens a novel avenue to fabricate efficient electrocatalysts for practical applications.

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