## ChemComm



**View Article Online** 

## COMMUNICATION



Cite this: Chem. Commun., 2014, 50, 11151

Received 25th May 2014, Accepted 23rd July 2014

DOI: 10.1039/c4cc03987d

www.rsc.org/chemcomm

From filter paper to porous carbon composite membrane oxygen reduction catalyst<sup>†</sup>

Wenxiu Yang,<sup>ab</sup> Yanling Zhai,<sup>ab</sup> Xiaoyu Yue,<sup>ab</sup> Yizhe Wang<sup>ab</sup> and Jianbo Jia\*<sup>ab</sup>

A novel type of porous carbon composite membrane (PCCM) based on the low-cost common filter paper *via* a simple route is reported. The obtained material exhibited excellent electrocatalytic activities toward the oxygen reduction reaction, high tolerance of methanol crossover, and durability in alkaline solution.

To promote the development and wide application of fuel cells, the study of efficient, cheap, stable, and green non-precious metal oxygen reduction reaction (ORR) catalysts is a top priority.<sup>1-3</sup> Over the past few years, tremendous efforts have been made toward developing a variety of carbon composites that possess relatively good electrocatalytic ORR activity to substitute the precious metal catalysts such as Pt and Pt-based materials.<sup>4-6</sup> In general, in the quest of developing high efficient carbon composite catalysts, several reports are available on different routes such as hydrothermal processes,<sup>7,8</sup> high-temperature pyrolysis,<sup>9,10</sup> microwave,<sup>11</sup> and chemical vapor deposition.<sup>12</sup> Over the past few decades, the materials, including carbon nanotubes,<sup>13</sup> fullerenes,<sup>14</sup> graphene,<sup>15,16</sup> mesoporous carbon,<sup>17,18</sup> carbon black,<sup>19</sup> polymers,<sup>20</sup> and organic metal frameworks<sup>7</sup> have been widely adopted as the carbon precursor to prepare carbon composites. However, it is a cockamamie procedure to prepare the special carbon nanostructures.<sup>21,22</sup> Hence, the batch synthesis of well-controlled and low-cost carbon composite ORR catalysts becomes one of the biggest challenges at present in the field of preparation of nonprecious metal ORR catalysts. To date, there has been tremendous interest in exploring a simple method to prepare stable carbon composites from renewable biomass resources, including soy milk, wood, bamboo, fruits, kenaf stem, egg white, and bacteria, for potential applications in supercapacitors, energy storage,





electroanalytical chemistry, and electrocatalysts.<sup>23–27</sup> In this work, we attempt to prepare a porous carbon composite membrane (PCCM) for the first time from low-cost common filter paper (FP) as the carbon precursor. Meanwhile, the resultant PCCM possesses efficient electrocatalytic activities for the ORR in an alkaline environment. The Fe-based nanoparticles formed on the composite surface during pyrolysis may further improve the electrocatalytic ORR activity of the PCCM, and the porous architecture of this FP-derived composite is beneficial for O<sub>2</sub> adsorption and transport during the ORR process. Illustration of the preparation of PCCM is presented in Scheme 1. The fabrication processes are given in the ESI.<sup>†</sup> For simplicity, the samples were denoted as the PCCM<sub>900</sub>-1% based on pyrolysis temperature (900 °C) and the concentration of Fe(NO<sub>3</sub>)<sub>3</sub> (1.0%), respectively.

For the purpose of comparing the morphological changes of the PCCM synthesized at different temperatures, we performed scanning electron microscopy (SEM) analysis. Fig. 1A clearly depicts the morphology of the PCCM<sub>800</sub>-1% after annealing at 800 °C; there are fewer pores or nanoparticles on the composite surface. The PCCM<sub>900</sub>-1% displayed in Fig. 1B possesses relatively homogeneous morphology with uniformly dispersed nanoparticles near or in the



Fig. 1 SEM images of (A) PCCM\_{800}-1%, (B) PCCM\_{900}-1%, and (C) PCCM\_{1000}-1%.

<sup>&</sup>lt;sup>a</sup> State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, P. R. China

<sup>&</sup>lt;sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, P. R. China. E-mail: jbjia@ciac.ac.cn; Tel: +86-431-85262251

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Experimental details, TEM, SEM, N\_2 adsorption isotherms, EDAX, and CVs are included. See DOI: 10.1039/c4cc03987d

pores; the diameters of the particles range from 30-100 nm. However, Fig. 1C shows that the diameter of the nanoparticles significantly increased and the nanoparticles aggregated for the PCCM<sub>1000</sub>-1% annealed at 1000 °C. Moreover, the surface of the PCCM<sub>1000</sub>-1% is no longer smooth or homogeneous. Transmission electron microscopy (TEM) results (Fig. S1, ESI<sup>+</sup>) of these materials are consistent with the SEM images. Fig. S2 (ESI<sup>†</sup>) shows the high-resolution TEM images obtained from the PCCM<sub>900</sub>-1%. The distances of 0.21 and 0.376 nm correspond to the (211) and (011) crystal planes of the Fe<sub>3</sub>C phase, respectively, and the Fe<sub>3</sub>C nanoparticles are surrounded by the carbon shells.<sup>3,28</sup> Fig. S3 (ESI<sup>+</sup>) exhibits the effect of Fe(NO<sub>3</sub>)<sub>3</sub> concentration on the morphology of PCCMs. Because oxidative gases, such as NO<sub>2</sub>, O<sub>2</sub>, and NO, will be released when Fe(NO<sub>3</sub>)<sub>3</sub> melts at high temperatures,<sup>29</sup> more pores appeared on the surface of the PCCM<sub>900</sub>-1% than on the surface of the PCCM<sub>900</sub>-0%. To obtain more information regarding the porous structure of the PCCM<sub>900</sub>-1%, the N<sub>2</sub> adsorption-desorption isotherm was measured, as exhibited in Fig. S4 (ESI<sup>†</sup>). The BJH desorption average pore width is 5.9 nm and the BET surface area is 297.1 m<sup>2</sup> g<sup>-1</sup>.

As presented in Fig. 2A, X-ray photoelectron spectroscopy (XPS) analysis indicates that PCCM<sub>900</sub>-1% is mainly composed of C (284.6 eV), O (532.5 eV), and Fe (711.5 eV), confirming that Fe was successfully doped into the carbon composite. In detail, the spectra of Fe 2p (Fig. 2B) of the PCCM<sub>900</sub>-1% reveal the distribution of Fe 2p into two species: Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  observed at 710.5 and 723.9 eV, respectively, from which we can deduce that iron atoms in the catalyst are either in the metallic, oxidized, or carbidic state.<sup>30</sup> Meanwhile, the energy dispersive X-ray analysis (EDAX) spectra (shown in Fig. S5D, ESI†) of the as-synthesized PCCM<sub>900</sub>-1% displayed the peaks corresponding to C (87.5%), O (5.55%), and Fe (6.95%) elements, which is consistent with the result of XPS. Furthermore, the PCCM<sub>900</sub>-1% was also characterized by thermogravimetric analysis (TGA); the result demonstrates an iron content of 11.54 wt% in the PCCM<sub>900</sub>-1% based on the remaining mass of



**Fig. 2** (A) XPS survey for the resultant PCCM<sub>900</sub>-1% and (B) high-resolution Fe 2p spectra. (C) The TGA curve of PCCM<sub>900</sub>-1% measured from 25 to 800 °C in air at a heating rate of 10 °C min<sup>-1</sup>. (D) XRD patterns of the PCCM<sub>900</sub>-1% and PCCM<sub>900</sub>-0%.

Fe<sub>2</sub>O<sub>3</sub> (16.49 wt%) as the temperature reached 700 °C (Fig. 2C), which is similar to that of the EDAX result. Fig. 2D describes the XRD patterns of the PCCM<sub>900</sub>-1% and PCCM<sub>900</sub>-0%. A typical broad peak at about  $2\theta$  = 25 corresponds to amorphous carbon substrates. Meanwhile, metallic, oxidized, and carbidic iron, such as Fe (JCPDS file: #894186), Fe<sub>3</sub>O<sub>4</sub> (JCPDS file: #892355), and Fe<sub>3</sub>C (JCPDS file: #893689) were present in the PCCM<sub>900</sub>-1%. Recent studies have verified that the encased Fe<sub>3</sub>C activates the surrounding graphitic layers, making the outer surface of the carbon layer active towards the ORR.<sup>3</sup> Therefore, the as-prepared PCCM with evenly dispersed Fe<sub>3</sub>C nanoparticles should find application in the ORR.

To explore the effect of the pyrolysis temperature and concentration of Fe(NO<sub>3</sub>)<sub>3</sub> on the electrocatalytic ORR activities of the PCCMs, a series of catalysts prepared under different conditions were examined; the results are given in Fig. S6 and S7 (ESI<sup>+</sup>). Compared with other modified electrodes, the PCCM<sub>900</sub>-1% modified glassy carbon electrode (PCCM900-1%/GCE) displays a superior ORR activity, which has a more positive reduction peak potential, onset potential, and higher reduction current density in O2saturated 0.10 M KOH. Meanwhile, Fig. S8 (ESI<sup>†</sup>) shows that the PCCM<sub>900</sub>-1%/GCE shows the best electron conductivity among the PCCMs produced with different amounts of Fe(NO<sub>3</sub>)<sub>3</sub>. This further proves that the porous morphology and uniformly dispersed Fe<sub>3</sub>C nanoparticles of the PCCM<sub>900</sub>-1% play an important role for the ORR. The kinetics of the ORR of the PCCM<sub>900</sub>-1%/GCE was further investigated and compared to the Pt/C/GCE by linear sweeping voltammograms at 1600 rpm using a rotating ring disk electrode (RRDE) (Fig. 3A). Note that the number of transferred electron (n) is calculated from the ring and disk currents, and is observed to be  $\sim$  3.82–3.97 in the entire potential range investigated (Fig. 3B). As shown in Fig. 3C, the H2O2 yield of the PCCM900-1%/GCE is below 17.3% over the potential range of -0.2 to -0.65 V in O<sub>2</sub>-saturated



**Fig. 3** (A) RRDE voltammograms of (a) PCCM<sub>900</sub>-1%/GCE and (b) Pt/C/GCE in O<sub>2</sub>-saturated 0.10 M KOH at a scan rate of 5 mV s<sup>-1</sup>, a rotation rate of 1600 rpm; the Pt ring electrode is polarized at 0.2 V (vs. Ag/AgCl). (B) Electron transfer number (*n*) and (C) H<sub>2</sub>O<sub>2</sub> yield of (a) PCCM<sub>900</sub>-1%/GCE and (b) Pt/C/GCE. (D) Current-time (*i*-*t*) chronoamperometric responses for the ORR on (a) PCCM<sub>900</sub>-1%/GCE and (b) Pt/C/GCE in O<sub>2</sub>-saturated 0.10 M KOH at -0.3 V at a rotation rate of 400 rpm.

0.10 M KOH, based on the assumption that oxygen reacts by a parallel mechanism.<sup>31</sup> All these conclusions indicate that the obtained PCCM<sub>900</sub>-1% possesses superior electrocatalytic ORR activity and that a four-electron transfer process predominates.

For the stability test, the PCCM<sub>900</sub>-1%/GCE and Pt/C/GCE toward ORR was examined chronoamperometrically in  $O_2$ -saturated 0.10 M KOH (at -0.3 V). As indicated in Fig. 3D, the PCCM<sub>900</sub>-1%/GCE still maintained 91.07% of its original activity after 20 000 s, whereas the Pt/C/GCE showed a decrease with a current loss of approximately 30.96%. Moreover, it could be observed that the addition of 1.0 M methanol to the  $O_2$ -saturated 0.10 M KOH has almost no influence on the electrocatalytic ORR activity of PCCM<sub>900</sub>-1%/GCE (Fig. S9, ESI†), whereas the Pt/C/GCE showed a pair of peaks corresponding to methanol oxidation under similar conditions. Overall, the high electrocatalytic ORR activity, excellent methanol crossover effect, and long-term stability of the PCCM<sub>900</sub>-1% make it a promising low-cost efficient ORR catalyst for fuel cells.

To verify the role of Fe<sub>3</sub>C nanoparticles in the ORR, a destructive test of the PCCM<sub>900</sub>-1% was performed. The Fe<sub>3</sub>C nanoparticles could be removed after grinding and leaching in hot acid.<sup>3</sup> As shown in Fig. S5A (ESI<sup>+</sup>), the surface of the g-PCCM<sub>900</sub>-1% is rough and almost all the nanoparticles disappear in the g-PCCM<sub>900</sub>-1% when compared with that of the PCCM<sub>900</sub>-1%. The corresponding EDAX spectra (Fig. S5C, ESI<sup> $\dagger$ </sup>) demonstrate that the g-PCCM<sub>900</sub>-1% is composed only of C and O elements. In addition, TEM images of ultrasonically dispersed PCCM900-1% and g-PCCM900-1% show that the nanostructure of the porous composites are similar (Fig. S1B and D, ESI<sup>+</sup>). The results indicated that iron was removed completely and the treatment of grinding and acid leaching did not cause an obvious change in the porous nanostructure of the g-PCCM<sub>900</sub>-1%. The polarization curves on the PCCM<sub>900</sub>-1%/GCE, g-PCCM<sub>900</sub>-1%/ GCE, and PCCM<sub>900</sub>-0%/GCE in O<sub>2</sub>-saturated 0.10 M KOH by RRDE are shown in Fig. S10 (ESI<sup>+</sup>). Compared with that of the PCCM<sub>900</sub>-1%/GCE, the peak current of the g-PCCM<sub>900</sub>-1%/GCE decreased significantly. Meanwhile, as displayed in Fig. S11 (ESI $^+$ ), the H<sub>2</sub>O<sub>2</sub> yield of the g-PCCM<sub>900</sub>-1%/GCE is 87.56-41.31% over the potential range of -0.2 to -0.65 V in O<sub>2</sub>-saturated 0.10 M KOH. Moreover, the number of transferred electrons is observed to be 2.24-3.17, which is similar to the PCCM<sub>900</sub>-0%/GCE. Therefore, the removal of Fe<sub>3</sub>C in PCCM changes the ORR mechanism from a four-electron to a twoelectron process. Recently, Bao and co-workers suggested that the carbon-encapsulated Fe catalyst could improve the ORR activity because of electron transfer from iron to the carbon layers, which leads to a decreased local work function on the carbon surface.32,33 Therefore, although the Fe<sub>3</sub>C nanoparticle was covered by the carbon layer, it plays a key role in the ORR, which improves the ORR efficiency by the synergetic interaction between the carbide and protective graphitic layers.<sup>3</sup> However, further studies are required to explain the detailed mechanism of ORR on the PCCM<sub>900</sub>-1%/GCE.

In summary, we have demonstrated a simple method for the fabrication of a novel PCCM electrocatalyst from a renewable, lowcost FP for the first time. The results indicated that the porous structure and the Fe-based nanoparticles greatly improved the electrocatalytic ORR activity of the PCCM. The  $Fe_3C$  nanoparticles that are covered by a carbon layer play a key role in the ORR through the synergetic interaction between the carbide and the protective graphitic layers. Therefore, the successful fabrication of PCCM not only promotes the development of a new porous carbon ORR catalyst, but this procedure is also more amenable to large-scale syntheses because of the cheap carbon precursor and the simple two-step synthetic process.

We acknowledge financial supports from the National Natural Science Foundation of China (No. 21305132), and the National Basic Research Program of China (No. 2010CB933603).

## Notes and references

- 1 S. Shanmugam and T. Osaka, Chem. Commun., 2011, 47, 4463-4465.
- 2 A. Morozan, P. Jegou, S. Campidelli, S. Palacin and B. Jousselme, Chem. Commun., 2012, 48, 4627–4629.
- 3 Y. Hu, J. O. Jensen, W. Zhang, L. N. Cleemann, W. Xing, N. J. Bjerrum and Q. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 3675–3679.
- 4 Y. J. Sa, C. Park, H. Y. Jeong, S. H. Park, Z. Lee, K. T. Kim, G. G. Park and S. H. Joo, *Angew. Chem., Int. Ed.*, 2014, **53**, 4102–4106.
- 5 J. P. Paraknowitsch and A. Thomas, *Energy Environ. Sci.*, 2013, **6**, 2839.
- 6 G. Nam, J. Park, S. T. Kim, D. B. Shin, N. Park, Y. Kim, J. S. Lee and J. Cho, *Nano Lett.*, 2014, 14, 1870–1876.
- 7 Y. Zhang, X. Bo, C. Luhana, H. Wang, M. Li and L. Guo, *Chem. Commun.*, 2013, **49**, 6885–6887.
- 8 Y. Tan, C. Xu, G. Chen, X. Fang, N. Zheng and Q. Xie, Adv. Funct. Mater., 2012, 22, 4584–4591.
- 9 Z. Zhang, G. M. Veith, G. M. Brown, P. F. Fulvio, P. C. Hillesheim, S. Dai and S. H. Overbury, *Chem. Commun.*, 2014, **50**, 1469–1471.
- 10 J. Jin, F. Pan, L. Jiang, X. Fu, A. Liang, Z. Wei, J. Zhang and G. Sun, ACS Nano, 2014, 8, 3313–3321.
- 11 S. K. Ramasahayam, U. B. Nasini, V. Bairi, A. U. Shaikh and T. Viswanathan, *RSC Adv.*, 2014, 4, 6306–6313.
- 12 L. Qu, Y. Liu, J.-B. Baek and L. Dai, ACS Nano, 2010, 4, 1321-1326.
- 13 S. Zhang, H. Zhang, Q. Liu and S. Chen, J. Mater. Chem. A, 2013, 1, 3302.
- 14 K. I. Ozoemena, S. A. Mamuru, T. Fukuda, N. Kobayashi and T. Nyokong, *Electrochem. Commun.*, 2009, **11**, 1221–1225.
- 15 Y. Wang, Y. Shao, D. W. Matson, J. Li and Y. Lin, ACS Nano, 2010, 4, 1790–1798.
- 16 W. Ding, Z. Wei, S. Chen, X. Qi, T. Yang, J. Hu, D. Wang, L.-J. Wan, S. F. Alvi and L. Li, Angew. Chem., Int. Ed., 2013, 52, 11755–11759.
- 17 X. Bo and L. Guo, Phys. Chem. Chem. Phys., 2013, 15, 2459-2465.
- 18 J. Duan, Y. Zheng, S. Chen, Y. Tang, M. Jaroniec and S. Qiao, *Chem. Commun.*, 2013, 49, 7705–7707.
- 19 G. Wu, K. L. More, C. M. Johnston and P. Zelenay, *Science*, 2011, 332, 443–447.
- 20 H. Matsumoto, S. Imaizumi, Y. Konosu, M. Ashizawa, M. Minagawa, A. Tanioka, W. Lu and J. M. Tour, ACS Appl. Mater. Interfaces, 2013, 5, 6225–6231.
- 21 M. Jahan, Q. Bao and K. P. Loh, J. Am. Chem. Soc., 2012, 134, 6707–6713.
- 22 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, ACS Nano, 2010, 4, 4806–4814.
- 23 H. Zhu, J. Yin, X. Wang, H. Wang and X. Yang, *Adv. Funct. Mater.*, 2013, 23, 1305–1312.
- 24 R. J. White, V. Budarin, R. Luque, J. H. Clark and D. J. Macquarrie, *Chem. Soc. Rev.*, 2009, **38**, 3401–3418.
- 25 L. Wang, Q. Zhang, S. Chen, F. Xu, S. Chen, J. Jia, H. Tan, H. Hou and Y. Song, *Anal. Chem.*, 2014, **86**, 1414–1421.
- 26 Y. Zhai, C. Zhu, E. Wang and S. Dong, Nanoscale, 2014, 6, 2964–2970.
- 27 C. Zhu, J. Zhai and S. Dong, Chem. Commun., 2012, 48, 9367-9369.
- 28 J. Su, Y. Gao and R. Che, Mater. Lett., 2010, 64, 680-683.
- 29 M. Sobiesiak, Adsorption, 2013, 19, 349-356.
- 30 J. Fournier, G. Lalande, R. Cote, D. Guay and J. P. Dodelet, *J. Electrochem. Soc.*, 1997, 144, 218–226.
- 31 M. Bron, P. Bogdanoff, S. Fiechter, I. Dorbandt, M. Hilgendorff, H. Schulenburg and H. Tributsch, *J. Electroanal. Chem.*, 2001, **500**, 510–517.
- 32 J. Wang, G. Wang, S. Miao, X. Jiang, J. Li and X. Bao, *Carbon*, 2014, 75, 381–389.
- 33 D. Deng, L. Yu, X. Chen, G. Wang, L. Jin, X. Pan, J. Deng, G. Sun and X. Bao, Angew. Chem., Int. Ed., 2013, 52, 371–375.