## Gallic acid-assisted synthesis of Pd uniformly anchored on porous N-

## rGO as efficient electrocatalyst for microbial fuel cells

Xiao-Tong Wu, Jie-Cheng Li, Qiu-Ren Pan, Nan Li, \* Zhao-Qing Liu, \*

School of Chemistry and Chemical Engineering/Guangzhou Key Laboratory for Environmentally Functional Materials and Technology/Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou 510006, P. R. China

Fax: 86-20-39366908; Tel: 86-20-39366908;

E-mail: <u>nanli@gzhu.edu.cn (N. Li);</u>

E-mail: lzqgzu@gzhu.edu.cn (Z. Q. Liu)



Figure S1. The FTIR of the as-synthesized samples .



Figure S2. The SEM images of different scales of as-synthesis (a,c) GN@Pd; (b,d) G@Pd-GA.

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
С(К)	82.99	94.38	0.55	0.28	3.601
N(K)	2.32	1.98	0.08	0.51	1.889
О(К)	4.47	2.32	0.13	0.99	1.663
Pd(L)	10.23	1.31	0.14	0.95	2.596

 Table S1.
 The quantification results of GN@Pd-GA.

**Table S2.** The open circuit potential and limit current density for different catalysts.

	Pt/C	GN@Pd-GA	G@Pd-GA	GN@Pd
Open circuit potential (V)	0.65	0.62	0.59	0.57
Limit current density (mA cm <sup>-2</sup> )	-4.51	-4.43	-4.03	-3.10



Figure S3. CV curves of GN@Pd-GA in different conditions.



Figure S4. LSV curves of Pd/C and the as-synthesized catalysts.



**Figure S5.** CV curves of as-synthesized catalysts under different scan rates, respectively are 50 mV s<sup>-1</sup>, 25 mV s<sup>-1</sup>, 10 mV s<sup>-1</sup>, 4 mV s<sup>-1</sup>, 3 mV s<sup>-1</sup>, 2 mV s<sup>-1</sup>.

	Pt/C	GN@Pd-GA	G@Pd-GA	GN@Pd
R <sub>s</sub> (ohm)	1.10	1.57	1.28	1.64
R <sub>ct</sub> (ohm)	1.69	2.90	2.21	3.41

Table S3. The quantification results of samples

Table S4. The highest power density calculated from Fig.7 (b).

	Pt/C	GN@Pd-GA	G@Pd-GA	GN@Pd
the highest power density (mW m <sup>-2</sup> )	406.65	391.06	286.34	215



**Figure S6**. (a) SEM image of  $GN@SiO_2$ ; (b) SEM image of GN which is the  $GN@SiO_2$  materials after KOH treatment.



**Figure S7**. The TG and DTG curves of N-rGO material. (where the dW/dT values dropped immediately at 577°C is the decomposition temperature of the N-rGO, and the weight of GN lost nearly 100% at 800°C indicates that the KOH can dissolve  $SiO_2$  completely.)

The samples were characterized by SEM before and after treatment of alkali. From Figure S6a, it is obviously to observe the SiO<sub>2</sub> spheres about 300 nm combined with rGO. Nevertheless, Figure S6b shows that the SiO<sub>2</sub> decorated on GN were dissolved and faded away by the corrosion of KOH. Moreover, the result of TG curves in Figure S7 exhibits the final residue of GN material approach zero, and the DTG curves also reveals a sharp drop at 577°C. Those evidences confirm the decomposition temperature of the GN and the KOH can remove SiO<sub>2</sub> completely.<sup>1-4</sup>



**re S8.** LSV curves of catalysts in a 0.1 M KOH solution at the scan rate of 5 mV s<sup>-1</sup> with 1600 rpm; (b) Electrochemical impedance spectroscopy curves

	GN-6h	GN-8h	GN-12h	GN-24h
R <sub>s</sub> (ohm)	0.7661	0.8002	0.8065	1.181
R <sub>ct</sub> (ohm)	1.774	1.326	2.321	2.834

Table S5. The resistence results of samples

As shown in Figure S8a, the LSV curves for carbon materials disposed by KOH in various time reveal that the electrochemical performance of GN keep unchanged but a little on the carbon-based material with the increasing of etching time. According to the recently reported work, KOH treatment for the preparation of activated carbon has been determined by the range of high temperature.<sup>5</sup> In our experiment, the temperature for etching SiO<sub>2</sub> is 70°C. Furthermore, combining with the results of EIS test in Figure S8b and Table S5, the imperceptible changes for the performance of graphite materials may be attributed to the internal resistance of the catalysts as treatment time increased.



**re S9**. The SEM images of (a) GN@Pd with gallic acid; (b)GN@Pd with ascorbic acid and (c) GN@Pd with citric acid by utilizing different kinds of small-molecule reductants.



**Figure S10**. CV and LSV curves of as-prepared materials; (c-d) the LSV curves of GN@Pd-ascorbic acid and GN@Pd-citric acid under various rotate speeds in 0.1 M KOH and O<sub>2</sub>-saturtated solution, respectively.

As shown in Figure S9, the as-prepared GN@Pd-GA, GN@Pd-ascorbic acid and GN@Pd-cirtic acid samples were characterized by SEM. Besides, rotating disk electrode (RDE) was employed to testify the ORR electrocatalytic activity in Figure S10. Notably, the as-prepared GN@Pd-GA exhibits excellent ORR activity and reduction current density compared to the GN@Pd-ascorbic acid and GN@Pd-cirtic acid in alkaline environment. Especially, the optimal proportion of new preparation GN@Pd-GA ( $\omega$ % =

10% Pd) exhibits better activity than other two kinds of materials. Clearly, the ascorbic acid and citric acid have weak ability and unstable structure to anchor Pd nanparticles on N-rGO, and thus weaken the synergistic effect between GN and Pd.



Figure S11. Raman pattern of rGO.

## References

- H. Qian, J. Tang, M. S. A. Hossain, Y. Bando, X. Wang, Y. Yamauchi, *Nanoscale*, **2017**, 9, 16264-16272.
- D. Zhou, L. Yang, L. Yu, J. Kong, X. Yao, W. Liu, Z. Xu, X. Lu, *Nanoscale*, 2015, 7, 1501-1509.
- M. Liu, X. Wang, D. Zhu, L. Li, H. Duan, Z. Xu, Z. Wang, L. Gan, *Chem. Eng.J.*, 2017, 308, 240-247.
- Y. Gao, L. Li, Y. Jin, Y. Wang, C. Yuan, Y. Wei, G. Chen, J. Ge, H. Lu, *Appl. Energ.*, 2015, 153, 41-47.
- S. Wu, G. Chen, N. Y. Kim, K. Ni, W. Zeng, Y. Zhao, Z. Tao, H. Ji, Z. Lee, Y. Zhu, Small, 2016, 12, 2376-2384.