Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2018

Supporting Information

Palladium nanoparticles anchored on the NCNTs@NGS with a

three-dimensional sandwich-stacked framework as an advanced

electrocatalyst for ethanol oxidation

Shuwen Li*, Honglei Yang*, Hai Zou, Ming Yang, Xiaodi Liu, Jun Jin and

Jiantai Ma

State Key Laboratory of Applied Organic Chemistry, Gansu Provincial Engineering

Laboratory for Chemical Catalysis, College of Chemistry and Chemical Engineering,

Lanzhou University, Lanzhou 730000, P. R. China

*Corresponding authors.

E-mail addresses: lishw@lzu.edu.cn (Shuwen Li)

yanghl@lzu.edu.cn (Honglei Yang)

1 Experimental section

1.1 Materials and Reagents

The multi-walled carbon nanotubes (CNTs) were purchased from Chengdu Organic Chemicals Co. Ltd (Chengdu, PR China). The graphene oxide (GO) was purchased commercially from Nanjing XFNANO Materials Tech Co. Ltd (Nanjing, PR China). Ultrapure water (Millipore System, 18.2 M Ω cm) was used as solvents. All chemical reagents which were used were bought commercially without further purification.

1.2 Sample characterization

Elemental analysis was conducted with a conventional combustion method (CHN, varioMLCRO) based on the burn-off mass of the sample and on the analysis of the evolved gases using a thermal conductivity detector. Inductive coupled plasma atomic emission spectrometer (ICP-OES) analysis was recorded on Perkin Elmer (Optima-4300DV). Raman spectra were carried out with inVia Reinishaw confocal spectroscopy with 633 nm laser excitation. X-ray diffraction (XRD) measurements were carried out at room temperature and performed on a Rigaku D/max-2400 diffractometer using Cu-K α radiation as the X-ray source. X-ray photoelectron spectroscopy (XPS) analysis was carried on PHI-5702 X-ray photoelectron spectrometer. The TEM images were obtained by Tecnai G² F³⁰ electron microscope operating at 300 kV, equipped with an energy-dispersive X-ray spectroscopy (EDX, TECNAI G2, USA) analyzer. The SEM images were obtained with a MIRA 3 XMU electron microscope. The Brunauer-Emmette-Teller (BET) surface area and pore size measurements of the catalyst were performed by N₂ adsorption/desorption analyses using a Tristar II 3020 instrument.

1.3 Electrochemical measurements

A standard three-electrode cell with a CHI model 660E electrochemical

workstation (Shanghai Chenhua Instrument Factory, China) was used to evaluate the electrochemical behavior of the catalysts. A platinum wire was used as the counter electrode and an Hg/HgO electrode as the reference. The working electrode was a glassy carbon electrode (GCE, diameter: 3.0 mm) carefully polished with Al₂O₃ powders (Aldrich, 0.05 mm) before each experiment. The working electrodes were prepared as follows. 4 mg of the sample was dispersed in 4 mL solution of double distilled water, ethanol and 0.5 wt% Nafion solution (9:9:2) with ultrasonic treatment to produce a homogeneous suspension. Then, the well-dispersed suspension (5 μ L) was drop-casted onto the glassy carbon electrode, which was then dried in air at room temperature. Adsorption of CO was performed by immersing the electrode into and bubbling CO through the solution for 15 min. Then, CO was purged from solution by N₂ bubbling for 10 min.

$$ECSA = \frac{Q_{\rm s}}{0.424 \times M_{\rm pd}} \text{ (Equation S1)}^{1,2}$$

Where $Q_{\rm S}$ (mC) is the total charge by the integral area of PdO reduction peak, the constant 0.424 (mC cm⁻²) is presumed for the reduction of PdO monolayer and $M_{\rm pd}$ is the Pd loading on the working electrode.

$$TOF = \frac{I_{\rm f}}{{\rm n}eN}$$
 (Equation S2)³

Where I_f is the current density, n is the number of electrons transferred for EOR, e is the elementary charge, and N is the atomic number per gram of palladium.

2 Figures and Tables



Fig. S1 SEM images and the scan range of elemental mappings of Pd/NGS (A1-A4), Pd/NCNTs (B1-B4) and Pd/NCNTs@NGS (C1-C4).



Fig. S2 HAADF-STEM image (A) and elemental mappings (B, C and D) of Pd/NCNTs@NGS.



Fig. S3 (A) Nitrogen adsorption-desorption isotherms and (B) the pore size distribution calculated by the Barrett-Joyner-Halenda (BJH) method of Pd/NCNTs, Pd/NGS and Pd/NCNTs@NGS.



Fig. S4 The XPS spectra of (A) N 1s for NCNTs@NGS and (B) Pd 3d for Pd/GS.

As a contrast, the Pd NPs was immobilized on the "pure" graphene (Pd/GS) used the same method. The graphene (GS) was prepared by a physical method was purchased from Nanjing XFNano Materials Tech Co., Ltd. There is almost no functional group on the surface of GS. Figure S1 shows the XPS spectra of (A) N 1s for NCNTs@NGS and (B) Pd 3d for Pd/GS. The binding energy of N 1s in the Pd/NCNTs@NGS was observe at 399.7 eV, which shifts negatively about 0.2 eV compared to that of NCNTs@NGS (399.5 eV). Moreover, the 3d_{5/2} and 3d_{3/2} for Pd(0) in the Pd/NCNTs@NGS was found at 335.8 eV and 341.1 eV, which distinctly positively shifts compared to that of Pd/GS (335.4 eV and 340.7 eV). The shifts in the binding energy of Pd and N may be attributed to the interactions between Pd nanoparticles and nitrogen-containing groups.

Gutul at a	\mathbf{P}_{1}
Catalysts	Pd content (wt.%)
Pd/NGS	9.87
Pd/NCNTs	9.31
Pd/NCNTs@NGS	9.68

Table S1 The Pd contents by ICP-OES analysis of as-prepared catalysts.

Catalysts	$I_{\rm f}({ m mA~mg^{-1}})^{\rm a}$	Reference
Pd/NCNTs@NGS	1823.2	This work
Ni@Pd-Ni nanowire	622	4
Pd-AA60	1160	5
Pd-NrGO hybrids	32.76	6
Pd/B-N-G	464.5	7
Pd-P/PDA-GS-2	1733.2	8
Mesoporous Pd film	1735.0	9
Pd/Ni(OH) ₂ /Rgo	1546	10
Pd-Pt@β-CD-RGO	1609	11
Core-shell Au-Pd ND	1200	12
NiPd	308.86	13
Pd TBTs/C	1590	14
PdNi/EGO	770.6	15
PdNi	1498.9	16
Pd-CeO _{2-x} /PDA-CNTs	1442.7	17
Pd@CoP NSs/CFC	1413.3	18
Pd_5Au_1	1739.93	19
Pd/NCNT	517	20
Pd/MnO ₂ /GNRs	1260	21
PdS _x /C	162.1	22
Pd ₃ Pb_HN72	480	23

 Table S2 Comparison of the electrocatalytic activity of this work with recent reports⁴⁻²³.

^aScan rate is 50 mV s⁻¹.

References

- R. Kumar, R. Savu, R. K. Singh, E. Joanni, D. P. Singh, V. S. Tiwari, A. R. Vaz, E. T. S. G. da Silva, J. R. Maluta, L. T. Kubota and S. A. Moshkalev, *Carbon*, 2017, 117, 137-146.
- 2. G. M. Alvarenga, I. B. Coutinho Gallo and H. M. Villullas, J. Catal., 2017, 348, 1-8.
- 3. H. Yang, Z. Yu, S. Li, Q. Zhang, J. Jin and J. Ma, J. Catal., 2017, 353, 256-264.
- 4. F. Guo, Y. Li, B. Fan, Y. Liu, L. Lu and Y. Lei, *ACS Appl. Mater. Interfaces*, 2018, **10**, 4705-4714.
- 5. N. Ma, X. Liu, Z. Yang, G. Tai, Y. Yin, S. Liu, H. Li, P. Guo and X. S. Zhao, ACS Sustainable Chem. Eng., 2018, 6, 1133-1140.
- R. Kumar, E. T. S. G. da Silva, R. K. Singh, R. Savu, A. V. Alaferdov, L. C. Fonseca, L. C. Carossi, A. Singh, S. Khandka, K. K. Kar, O. L. Alves, L. T. Kubota and S. A. Moshkalev, *J. Colloid Interface Sci.*, 2018, 515, 160-171.
- 7. Y. Jin, D. Han, W. Jia, G. Huang, F. Li, X. Chen, R. Li, M. Zheng and W. Gao, J.

Electrochem. Soc., 2017, 164, F638-F644.

- 8. H. Yang, H. Zou, M. Chen, S. Li, J. Jin and J. Ma, *Inorg. Chem. Front.*, 2017, 4, 1881-1887.
- M. Iqbal, C. Li, K. Wood, B. Jiang, T. Takei, Ö. Dag, D. Baba, A. S. Nugraha, T. Asahi, A. E. Whitten, M. S. A. Hossain, V. Malgras and Y. Yamauchi, *Chem. Mater.*, 2017, 29, 6405-6413.
- H. Wenjing, M. Xian Yin, W. Han, F. Renfei, Z. Jigang, D. P. N., Z. Peng, C. Fengjiao, H. Na, Z. Feipeng, Z. Junhua, C. Wen Bin and L. Yanguang, *Adv. Mater.*, 2017, 29, 1703057.
- 11. X. Ran, L. Yang, Q. Qu, S. Li, Y. Chen, L. Zuo and L. Li, *RSC Adv.*, 2017, 7, 1947-1955.
- 12. G. Su, H. Jiang, H. Zhu, J.-J. Lv, G. Yang, B. Yan and J.-J. Zhu, *Nanoscale*, 2017, **9**, 12494-12502.
- 13. S. C. Sarma, U. Subbarao, Y. Khulbe, R. Jana and S. C. Peter, *J. Mater. Chem. A*, 2017, **5**, 23369-23381.
- 14. S. Changshuai, H. Wei, G. Yaxiao, W. Jin and W. Erkang, Chem-Eur. J., 2017, 23, 5799-5803.
- J. L. Tan, A. M. De Jesus, S. L. Chua, J. Sanetuntikul, S. Shanmugam, B. J. V. Tongol and H. Kim, *Appl. Catal.*, *A*, 2017, **531**, 29-35.
- Y. Feng, D. Bin, B. Yan, Y. Du, T. Majima and W. Zhou, J. Colloid Interface Sci., 2017, 493, 190-197.
- H. Yang, Q. Zhang, H. Zou, Z. Song, S. Li, J. Jin and J. Ma, *Int. J. Hydrogen Energy*, 2017, 42, 13209-13216.
- 18. S.-H. Ye, J.-X. Feng and G.-R. Li, ACS Catal., 2016, 6, 7962-7969.
- J. Zhong, D. Bin, Y. Feng, K. Zhang, J. Wang, C. Wang, J. Guo, P. Yang and Y. Du, *Catal. Sci. Technol.*, 2016, 6, 5397-5404.
- D. Hiltrop, J. Masa, A. Maljusch, W. Xia, W. Schuhmann and M. Muhler, *Electrochem. Commun.*, 2016, 63, 30-33.
- 21. Q. Liu, K. Jiang, J. Fan, Y. Lin, Y. Min, Q. Xu and W.-B. Cai, *Electrochim. Acta*, 2016, **203**, 91-98.
- 22. Q. Zhang, F. Zhang, X. Ma, Y. Zheng and S. Hou, J. Power Sources, 2016, 336, 1-7.
- 23. R. Jana, U. Subbarao and S. C. Peter, J. Power Sources, 2016, 301, 160-169.