



# Microwave-assisted Synthesis of Pd Oxide-rich Pd Particles on Nitrogen/Sulfur Co-Doped Graphene with Remarkably Enhanced Ethanol Electrooxidation

J. X. Zhang<sup>1</sup>, X. L. Yang<sup>1\*</sup>, H. F. Shao<sup>2</sup>, C. C. Tseng<sup>1</sup>, D. S. Wang<sup>1</sup>, S. S. Tian<sup>1</sup>, W. J. Hu<sup>1</sup>, C. Jing<sup>1</sup>, J. N. Tian<sup>1</sup>, Y. C. Zhao<sup>1\*</sup>

<sup>1</sup> College of Chemistry and Pharmacy, Guangxi Normal University, Guilin 541004, PR China

<sup>2</sup> Shandong Non-Metallic Materials Institute, Jinan 250031, PR China

Received September 01, 2016; accepted November 18, 2016; published online December 19, 2016

## Abstract

Nitrogen and sulfur co-doped graphene supported Pd oxide-rich (PdO<sub>x</sub>-rich) Pd nanoparticles (Pd/NS-rGO) are synthesized by microwave-assisted ascorbic acid reduction method. Raman spectrum reveals that the introduced NS co-doping could introduce more defects on the graphene surface. X-ray diffraction, X-ray photoelectron spectrum, SEM and TEM images indicate that the synthesized PdO<sub>x</sub>-rich Pd particles are well-dispersed on NS co-doped graphene surface. Cyclic voltammograms curves illustrate that the Pd/NS-rGO catalyst exhibits a larger electrochemically active surface

area (35.7 m<sup>2</sup> g<sup>-1</sup>) and higher positive current density (1,054.0 mA mg<sup>-1</sup> Pd) than other catalysts prepared by similar methods. The Pd/NS-rGO catalyst also reveals superior anti-poisoning intermediate species ability and amazing stability. The electrocatalytic mechanism is also detailedly discussed and the designed Pd/NS-rGO catalyst has opened up a new insight and methodology for the construction of a high performance and stability ethanol electrocatalysts in corrosive alkaline environments.

**Keywords:** Direct Ethanol Fuel Cells, Electrocatalysis, Microwave-assisted, NS Co-doped Graphene, Pd Particles

## 1 Introduction

With the rapid increase in energy demand and growing concerns about environmental pollution, research on renewable and green energy sources has attracted considerable interest in the past decades [1–4]. Amongst various candidates, direct ethanol fuel cells (DEFCs) possess notable features including simple design, easy storage, good stability, high energy conversion efficiency, environmental-friendly character and low proton exchange membrane permeability, etc. [5–7]. Those characteristics continually soar the global attention to DEFCs to new highs. In addition, the kinetics of ethanol oxidation in alkaline medium is faster and DEFCs tend to be less corrosive than those in acidic medium [8–11]. Despite the significant advantages, there are still some major drawbacks for DEFCs. The complete oxidation of ethanol is extremely diffi-

cult and involves in some complex mechanism, such as cleavage of C-C bond, transference of 12 electrons and elimination of CO, CH<sub>x</sub>-intermediates, which will poison the catalyst [12, 13]. Therefore, it is of great importance to design economic electrocatalysts with improved electrocatalytic performance, kinetic efficiency and stability [14, 15]. However, the low abundance and easy poisoning properties of platinum-related catalysts have seriously hindered their commercial applications in fuel cells [16, 17]. Alternatively, theoretical and experimental investigations demonstrated that Pd-based catalysts could overcome these obstacles and have aroused tremendous attention [18, 19]. Although Pd particles show good catalytic behav-

[\*] Corresponding author, xiulin.yang@kaust.edu.sa, yanchunzhao@aliyun.com

iors for many useful reactions under different reaction conditions, the particles are prone to aggregation and form Pd black because of their high surface energy [20,21]. Therefore, the immobilization of Pd particles on various supports is regarded as one of the most practical ways to address this problem.

Over the past decade, graphene has triggered tremendous interest due to its high electron mobility, excellent mechanical flexibility, specific surface area and unique optical properties [22,23]. But most of the pristine graphene are subjected to chemical inertness and it remains urgent to modify the chemical properties of graphene by functionalization or surface modification to expand its application [24,25]. Recently, heteroatom doping of graphene displays exceptional properties and characteristics. In the process of substitutional doping, carbon atoms in the skeleton are replaced by heteroatoms and the graphene structure are destroyed [26,27]. Up to now, many techniques have been developed to obtain heteroatom-doped graphene, in which solvothermal and hydrothermal treatments are deemed to be a most facile and economic way to synthesize heteroatoms doped graphene [28]. It is interesting to note that introduction of nitrogen and sulfur, both with rich electrons, can change the p-conjugated system of graphene and alter the carbon structures. This will it will generate more defects and nuclear sites which can act as anchoring sites for metal particles [29], and then strengthen the interaction between metal particles and graphene supports and benefit the transformation of electron from supports to metal catalysts [30]. Currently, most of the published NS-doped carbon materials show superb performance in oxygen reduction reactions, formic acid oxidation, Li-ion batteries, etc. [31–33]. Until now, only few papers related to noble metals on NS co-doped graphene for alkaline ethanol electro-oxidation are published.

In this paper, we present a facile route to prepare NS dual-doped graphene by using ammonium chloride and sodium thiocyanate as precursors, and subsequently conduct microwave-assisted ascorbic acid reduction to prepare a highly dispersed PdO<sub>x</sub>-rich Pd/NS-rGO catalyst. The introduction of N and S in graphene structure could generate abundant active sites for well-dispersing PdO<sub>x</sub>-rich Pd particles on NS functionalized graphene surface. The synthesized Pd/NS-rGO catalyst exhibits larger electrochemically active surface area (EAS, 35.7 m<sup>2</sup> g<sup>-1</sup>) and higher positive current density (1,054.0 mA mg<sup>-1</sup> Pd) than other similar method prepared catalysts. In addition, the Pd/NS-rGO catalyst also reveals superior anti-poisoning intermediate species ability and amazing stability.

## 2 Experimental

### 2.1 Preparation of GO and Reduced-GO

A modified Hummers method was used to prepare Graphene oxide (GO). Briefly, graphite powder (1.0 g) and NaCl (20.0 g) were thoroughly mixed by milling in mortar for 30 min. After rinsed with deionized water, the mixture was dried overnight at 60 °C, then added H<sub>2</sub>SO<sub>4</sub> (98%) to the dried

material and stirred the mixture for 24 h at room temperature. Subsequently, KMnO<sub>4</sub> (0.5 g) was slowly added into the mixture with stirring at 40 °C for 30 min. Then, the mixture was diluted with 140 mL deionized water at ambient temperature. One hour later, another H<sub>2</sub>O (140 mL) and H<sub>2</sub>O<sub>2</sub> (10 mL) was added into the mixture. Upon treatment with peroxide, the suspension was centrifuged, washed and dried overnight to obtain GO. The prepared GO was then put into a furnace and kept at 700 °C in N<sub>2</sub> for 1 h. The reduced-GO (rGO) was obtained and left for further treatment.

### 2.2 Synthesis of NS-rGO

rGO (30 mg), NaSCN (160 mg), NH<sub>4</sub>Cl (106 mg) were dispersed in distilled water under ultrasonic treatment. Then, the

dropped to fix the catalysts on GCE. All the potentials are referred to the saturated calomel electrode (SCE) in this work. A Pt foil and SCE were employed as a counter electrode and a reference electrode, respectively. The cyclic voltammogram (CV) measurement was firstly carried out in a solution of 0.5M NaOH at a scan rate of 50 mV s<sup>-1</sup> from 0.8 V to 0.4 V, in order to calculate the electrochemical active surface areas (EAS) of the catalysts. Afterwards, electrooxidation of ethanol was investigated by CV measurements with the same scan rate between 0.8 V to 0.4 V in a solution of 0.5M NaOH + 1.0M C<sub>2</sub>H<sub>5</sub>OH. Chrono-ampereometry measurements were then performed at a fixed potential of 0.2 V for 7,200 s in 0.5M NaOH + 1.0M C<sub>2</sub>H<sub>5</sub>OH solution. The metal loading was kept at 70.8 mg cm<sup>-2</sup> and all tests were conducted at ambient temperature (25 ± 0.5 °C).

### 3 Results and Discussion

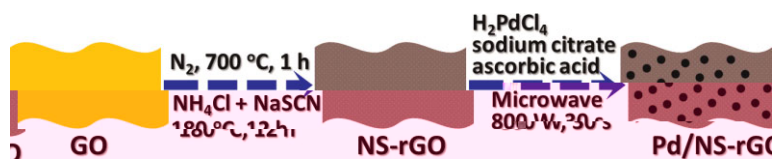
The NS dual-doped graphene was synthesized via hydrothermal treatment of the obtained rGO from GO together with NaSCN and NH<sub>4</sub>Cl in water solution, as illustrated in Scheme 1. The hydrothermal treatment could induce the thermal decomposition of NaSCN and NH<sub>4</sub>Cl at high temperature and pressure conditions. The generated fragments of N and S will strongly attack the structure of graphene, and the formed different groups will be effectively functionalized or non-functionalized on the graphene structures. The NS dual-doped graphene was then ultrasonically mixed with H<sub>2</sub>PdCl<sub>4</sub>, sodium citrate and ascorbic acid at room temperature. The sodium citrate is used as stabilizing agent and the ascorbic acid is regarded as reducing agent. The mixed solution was then put into microwave reactor in a beaker at a power of 800 W for 30 s. The microwave reactor could rapidly increase the temperature of the mixture solution, promote dispersion of solutes and accelerate the completion of the whole reaction.

Raman spectroscopy was used to gauge the extent of disorder and degree of the prepared NS-rGO and rGO. As shown in Figure 1A, there are two distinct peaks including G-band with E<sub>2g</sub> symmetry roughly located at 1,581 cm<sup>-1</sup> ascribed to ordered sp<sup>2</sup> hybridized graphitic carbon atoms and D-band with A<sub>1g</sub> symmetry at about 1,354 cm<sup>-1</sup> arising from disordered sp<sup>3</sup> defect sites, amorphous carbon or edges defects, etc. [34]. The intensity of I<sub>D</sub>/I<sub>G</sub> reflects the structure defects and edge plane exposure, and it is usually adopted to evaluate the doping and defects in carbon materials. A higher ratio of I<sub>D</sub>/I<sub>G</sub> indicates higher defects, and lower value signifies lower disorder in the graphitic lattice. It can be clearly seen that the I<sub>D</sub>/I<sub>G</sub>

ratio of NS-rGO (0.99) is larger than that of rGO (0.57). On the other hand, it is well known that the D<sub>t</sub>-band is also associated with defects and disorder in carbon structure [35]. Thus, the largest I<sub>D</sub>/I<sub>G</sub> ratio and the enhancement of the D<sub>t</sub>-band of the NS-rGO imply that NS-rGO contains more amorphous carbon impurities than rGO [36]. In this case, those defects will in turn act as active sites and reinforce the interaction between Pd particles and support, and thus increase the catalysts loading and particles dispersion.

X-ray diffraction (XRD) was used to monitor the crystal structures of Pd/NS-rGO together with Pd/N-rGO, Pd/CNTs and Pd/XC-72. As shown in Figure 1B, all samples displayed five similar diffraction peaks at 2θ of approximately 40.1°, 46.7°, 68.1°, 82.1° and 86.6°, which can be well indexed to face-centered cubic (fcc) crystalline Pd (JCPDS: 65-2867) [37, 38]. It should be noted that, compared to Pd/N-rGO, Pd/CNTs and Pd/XC-72, Pd/NS-rGO shows several additional peaks which can be ascribed to the tetragonal structure of PdO (JCPDS: 43-1024). It means that the support of NS-rGO is much more beneficial to form PdO composition than others. This can be explained that the groups of N, S on rGO have a stronger binding force with Pd precursor, and thus it could suppress the reduction of the precursor to some extent. After microwave heating treatment, the resulted high temperature is more tending to form PdO composition. In addition, a narrow peak around 26° for Pd/NS-rGO can be assigned to the (002) characteristic diffraction peak of hexagonal crystalline graphite [39], which is consistent with Pd/CNTs composite. However, there is a broad peak at ca. 24.9° on Pd/N-rGO, which is a typical characteristics of stacked graphene layers with short-range order [40]. The different crystal degree of the substrates and the different forms of Pd existence indicate that the co-doped N/S plays an important role in the preparation of PdO<sub>x</sub>-rich Pd/NS-rGO catalyst.

The scanning electron microscope (SEM) image of Pd/NS-rGO composite is shown in supporting Figure S1. It can be seen that the particles of Pd are randomly distributed over the whole area of NS dual-doped graphene and almost no agglomeration of Pt particles can be seen. The transmission electron microscope (TEM) image in Figure 2A shows that the NS co-doped graphene exhibits an extremely thin silk veil waves-like morphology and almost none significant stacking of graphene is observed. This reveals that graphite is effectively exfoliated by the modified Hummer's method. Besides, the translucent graphene nanosheets display some defects and partially crinkled nature, which may originate from the defective structure formed during the fabrication of GO and the heteroatom doping processes [41]. These defects can facilitate the chemisorption of reactants and well disperse the reduced metal particles. It can be seen that the reduced particles are uniformly dispersed with sphere-like shape and some of them coexist like nanocluster structures on the NS-rGO nano-framework support. The high-resolution TEM image in Figure 2B shows that there are two types of lattice fringes with 0.225 nm and 0.264 nm with respect to



Scheme 1 Schematics of the synthetic procedures for the Pd/NS-rGO catalyst.

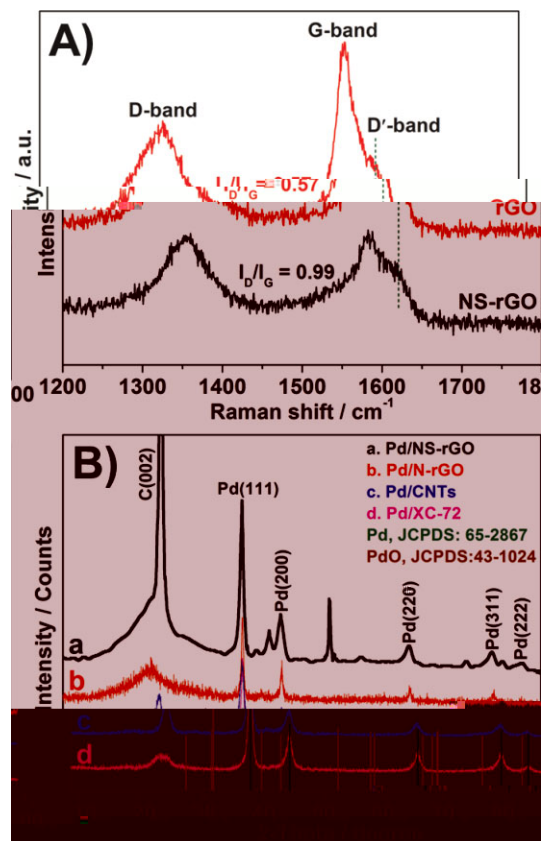


Fig. 1 (A) Raman spectra of rGO and NS-rGO. (B) XRD patterns of Pd/NS-rGO, Pd/N-rGO, Pd/CNTs and Pd/XC-72.

Pd (111) and PdO (101) presented on the catalyst's surface. As shown in Figure 2C, the mean size of the metal nanoparticles on NS-rGO support is obtained by measuring 200 randomly chosen particles from the magnified TEM image. For the PdO<sub>x</sub>-rich Pd catalyst, the mean particle size has a broad distribution (3–9 nm) with an average diameter of approximately 5.4 nm. Inductively coupled plasma (ICP) was used to measure the metal loadings of various catalysts. The result shows that the loading content of Pd on NS-rGO is 19.2 wt.%, which is similar with other three compared catalysts (see Supporting Table S1). For better understanding the effect of morphologies on catalytic performance, the TEM images of other compared catalysts are further characterized as shown in Supporting Figure S2–S4. For the Pd/N-rGO catalyst, the particles distribute in two different ranges, and the average particles sizes are ~4.7 nm and ~16.8 nm, respectively. However, for the metal particles on CNTs and XC-72 carbon black, a large number of aggregated particles could be observed on their surface, and these aggregated particles may greatly affect their electrocatalytic performance improvement.

X-ray photoelectron spectrum (XPS) is performed to gain insight into the chemical state and surface composition of Pd, N and S in the Pd/NS-rGO sample. As shown in Supporting Figure S5, the full XPS spectrum includes C 1s, O 1s, N 1s, S 2p and Pd 3d peaks, which indicate that the elements of N and S are successfully incorporated into graphene networks. A sharp

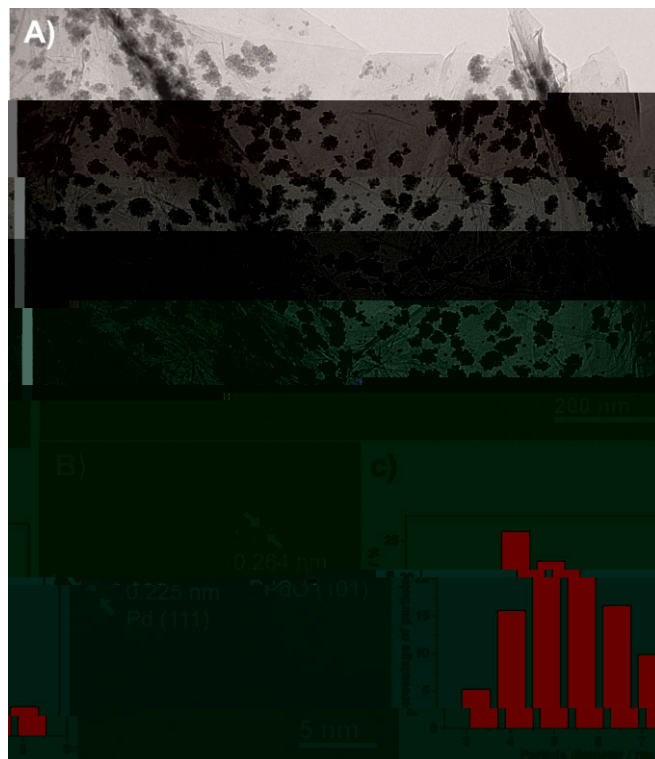


Fig. 2 (A) TEM image, (B) high-resolution TEM image and (C) particle size distribution of Pd/NS-rGO composite.

high peak observed at ~284.4 eV certifies the existence of carbon atoms, and most of which are sp<sup>2</sup> hybrid carbons arranged in a conjugated honeycomb lattice of graphene. The elemental contents of N and S in Pd/NS-rGO are calculated for 2.98% and 1.82%, respectively. As shown in Figure 3A, the high-resolution spectrum of N 1s in NS-rGO could be fitted by two peaks as for pyridine-like N (398.7 eV) and pyrrole-like N (400.8 eV) species [42]. Pyridinic N bonds with two sp<sup>2</sup> carbon atoms at the defects or edges of graphene can provide the p-system with one p electron, while pyrrolic N bonds with three sp<sup>2</sup> C atoms can contribute two p electron to the p-system, changing the valence band structure of graphene [43]. The high-resolution of S 2p peak could be fitted with three different sulfur moieties (Figure 3B). It can be seen that the two peaks of binding energies at 162.1 eV and 167.6 eV can be assigned to the reduced (–SH) and oxidized (–SO<sub>n</sub>) sulfur moieties, respectively [44]. Additionally, another two small peaks at 163.7 eV and 165.1 eV could be clearly detected, which are in agreement with the ever reported S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> positions of thiophene-S owing to their spin-orbit coupling [41]. It is generally considered that co-doped two-types N and sulfur are responsible for the interaction with metal catalysts and prevent them from aggregation together [31].

The high-resolution Pd 3d photoelectron peaks of Pd/NS-rGO catalyst are presented in Figure 3C, the binding energies for Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> could be resolved into three doublets. The doublet peaks with binding energies of 335.6 eV (Pd 3d<sub>5/2</sub>) and 340.9 eV (Pd 3d<sub>3/2</sub>) are attributed to

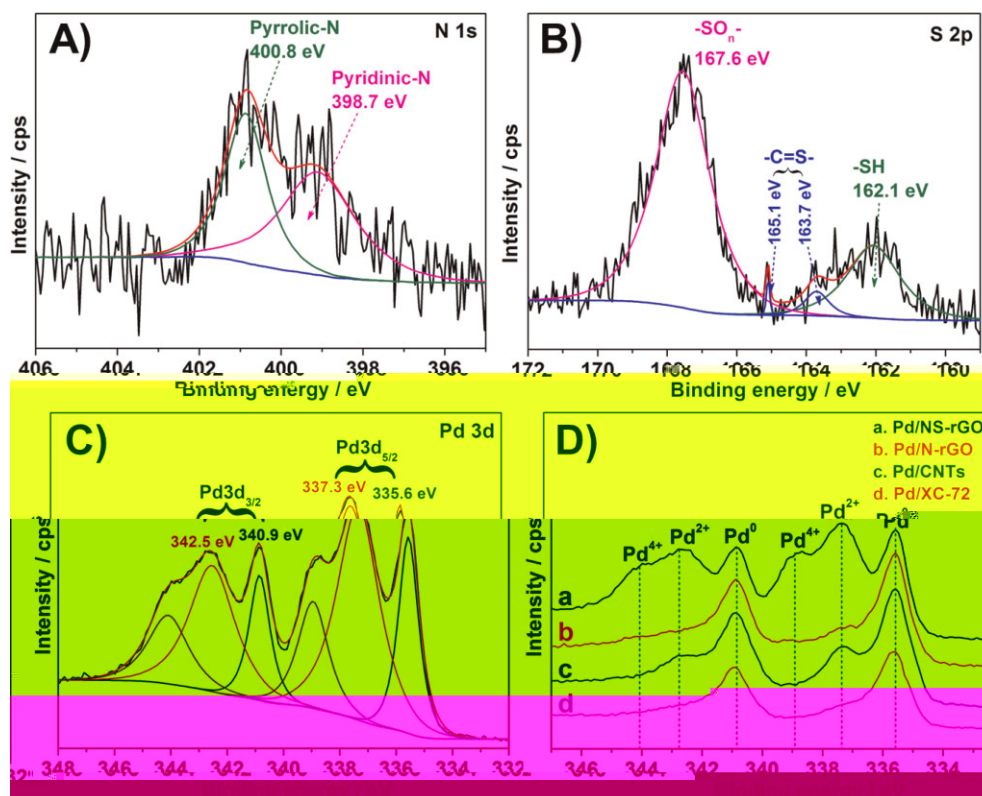


Fig. 3 High-resolution XPS spectra of (A) N 1s, (B) S 1s and (C) Pd 3d of Pd/NS-rGO. (D) Comparison of the sub-spectra of Pd 3d orbital from different catalysts.

metallic Pd [45]. The other doublet peaks with binding energies at 337.3 (Pd 3d<sub>5/2</sub>) and 342.5 eV (Pd 3d<sub>3/2</sub>) can be assigned to Pd<sup>2+</sup> in PdO [46], and the binding energies at 338.9 eV (Pd 3d<sub>5/2</sub>) and 344.1 eV (Pd 3d<sub>3/2</sub>) are corresponding to PdO<sub>2</sub> species [47]. The spectrum of Pd 3d indicates that the oxide of Pd (including PdO and PdO<sub>2</sub>) is predominant in the Pd/NS-rGO composite with a relative abundance accounting for 75.7% of the total metal Pd loading, which is ~3.1-fold higher than the Pd in the form of metal Pd. Interestingly, as shown in Figure 3D, the compared four catalysts exhibit similar binding energies for Pd<sup>0</sup> and Pd<sup>2+</sup>. It is a different phenomenon that only the as-synthesized Pd/NS-rGO sample shows the form of PdO<sub>2</sub> at higher binding energies. The strongest peak intensities for PdO and PdO<sub>2</sub> in Pd/NS-rGO catalyst illustrate that the co-doped N/S in the composite has a strong interaction force with the precursor of Pd under the same reduction conditions.

Cyclic voltammograms (CV) are executed to evaluate the electrochemical activity of Pd/NS-rGO, Pd/N-rGO, Pd/CNTs and Pd/XC-72 catalysts in N<sub>2</sub>-saturated 0.5M NaOH solution. As shown in Figure 4A, CV curves of the different catalysts are investigated in the range of 0.8 V to 0.4 V at a scan rate of 50 mV s<sup>-1</sup>. It can be seen that all catalysts have similar curve profiles and exhibit a very distinct reduction peaks at ~ 0.38 V. The reduction peaks could be ascribed to the transformation of PdO to metal Pd<sup>0</sup> [48], and the required coulomb charges could be used to estimate the electrochemically active

surface area (EAS) of the catalysts. Generally, the coulomb charges are assumed to be the electrochemical reduction of a closed-packed monolayer of PdO on the catalyst's surface (PdO + 2H<sup>+</sup> + 2e<sup>-</sup> → Pd + H<sub>2</sub>O) [49]. The EAS is estimated using the equation EAS = Q/SL [50], where Q is the charge of electrochemical reduction of PdO in microcoulomb (mC), S (405 mC cm<sup>-2</sup>) represents the proportionality constant which stands for the charge required to reduce monolayer of PdO, and L is the total amount of Pd (g) on the electrode. The calculated EAS results are listed in Table 1, and it is obviously revealed that the EAS value of Pd/NS-rGO is much larger than the ones of the other compared catalysts. The improved EAS value can be ascribed to the appearance of well-dispersed PdO<sub>x</sub>-rich Pd on NS-rGO support and could expose much more active sites than others for interface reactions [51].

The high EAS value is generally supported by high electrocatalytic activity. Figure 4B shows the CV curves of Pd/NS-rGO together with Pd/XC-72, Pd/N-rGO and Pd/CNTs catalysts in 0.5M NaOH + 1.0M C<sub>2</sub>H<sub>5</sub>OH solution with a scan rate of 50 mV s<sup>-1</sup>. It can be observed from CV curves that all onset potentials of the ethanol electro-oxidation begin at ~ 0.70 V, and the peak potentials of ethanol oxidation are in the range of 0.17 to 0.22 V for positive-going potential scan. In the forward-going scan, the oxidation peak is corresponding to the oxidation of freshly chemisorbed species coming from ethanol adsorption [52]. The reverse scan peak is primarily associated with removal of carbonaceous

species not completely oxidized in the forward-going scan than the oxidation of freshly chemisorbed species [53,54]. Bianchini et al. using In situ FTIR spectroscopic techniques

that all catalysts initially display a sharp current density decay, and then turn into a pseudo-steady state. As shown the insert chart in Figure 5, it could be observed that the current density of Pd/NS-rGO catalyst is 109.5 mA mg<sup>-1</sup> Pd after running 7,200 s, which is 1.84, 3.40 and 1.53-fold higher than Pd/N-rGO, Pd/CNTs and Pd/XC-72, respectively. The admirable stability of Pd/NS-rGO catalyst could be regarded relevant with well-dispersed Pd particles, the stronger binding force between Pd and co-doped N and S to inhibit agglomeration of particles, and rich-PdO<sub>x</sub> provided lots of adsorption hydroxyl to remove intermediate species.

## 4 Conclusions

In this work, we have demonstrated a facile process to synthesize NS co-doped graphene supported PdO<sub>x</sub>-rich Pd electrocatalysts via microwave-assisted ascorbic acid reduction method. The NS co-doped graphene provide uniformly active sites to deposited PdO<sub>x</sub>-rich Pd particles. The stronger binding force between PdO<sub>x</sub>-rich Pd particles and the support successfully suppressed the particles exfoliation and agglomeration after long-time stability testing. In addition, the Pd/NS-rGO catalyst also revealed a larger electrochemically active surface area, higher forward current density and tolerance to intermediate species poisoning. The well-dispersed PdO<sub>x</sub>-rich Pd particles on NS co-doped graphene in this study possess excellent electrocatalytic properties and stability for ethanol electrooxidation in alkaline media and may be of great potential regarding ethanol sensor and direct ethanol fuel cells.

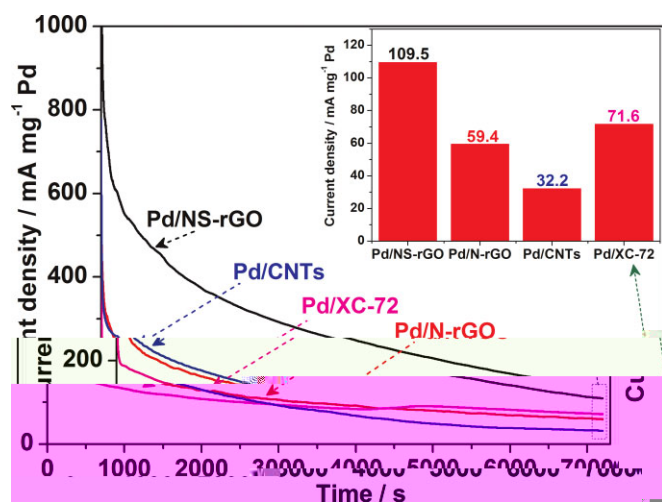


Fig. 5 Long-term stability curves of the Pd/NS-rGO, Pd/N-rGO, Pd/CNTs and Pd/XC-72 catalysts at  $-0.2$  V for 7,200 s in 0.5M NaOH + 1.0M C<sub>2</sub>H<sub>5</sub>OH solution. The inset image shows the last values of chronoamperometric curves for these four catalysts.

## Acknowledgements

This work has been supported by the National Natural Science Foundation of China (21163002, 21165004, 21363003), Natural Science Foundation of Guangxi Province (2014GXNSFFA118003, 2014GXNSFGA118008), BAGUI scholar program (2014A001), Project of Talents Highland of Guangxi Province and Guangxi Key Laboratory of Low Carbon Energy Materials.

## References

- [1] X. Huang, Z. Zhao, L. Cao, Y. Chen, E. Zhu, Z. Lin, M. Li, A. Yan, A. Zettl, Y. M. Wang, X. Duan, T. Mueller, Y. Huang, *Science* 2015, 348, 1230.
- [2] D. Wang, H. L. Xin, R. Hovden, H. Wang, Y. Yu, D. A. Muller, F. J. DiSalvo, H. D. Abruña, *Nat. Mater.* 2013, 12, 81.
- [3] Z. Yin, B. Chen, M. Bosman, X. Cao, J. Chen, B. Zheng, H. Zhang, *Small* 2014, 10, 3537.
- [4] G. Wang, L. Zhang, J. Zhang, *Chem. Soc. Rev.* 2012, 41, 797.
- [5] C. W. Xu, H. Wang, P. K. Shen, S. P. Jiang, *Adv. Mater.* 2007, 19, 4256.
- [6] E. Antolini, *Energy Environ. Sci.* 2009, 2, 915.
- [7] Y. Feng, L. Bu, S. Guo, J. Guo, X. Huang, *Small* 2016, 12, 4464.
- [8] K. Tran, T. Q. Nguyen, A. M. Bartrom, A. Sadiki, J. L. Haan, *Fuel Cells* 2014, 14, 834.
- [9] H. Takahashi, M. Sagihara, M. Taguchi, *Int. J. Hydrog. Energy* 2014, 39, 18424.
- [10] Z. Chen, D. Higgins, A. Yu, L. Zhang, J. Zhang, *Energy Environ. Sci.* 2011, 4, 3167.
- [11] V. Rao, Hariyanto, C. Cremers, U. Stimming, *Fuel Cells* 2007, 7, 417.
- [12] S. Beyhan, J.-M. L. ger, F. Kadrgan, *Appl. Catal. B-Environ.* 2013, 130–131, 305.
- [13] W. Du, N. A. Deskins, D. Su, X. Teng, *ACS Catal.* 2012, 2, 1226.
- [14] Y.-h. Li, Q.-z. Xu, Q.-Y. Li, H. Wang, Y. Huang, C.-w. Xu, *Electrochim. Acta* 2014, 147, 151.
- [15] B. Liu, Z. W. Chia, Z. Y. Lee, C. H. Cheng, J. Y. Lee, Z. L. Liu, *Fuel Cells* 2012, 12, 670.
- [16] J. J. Li, J. S. Wang, X. Guo, J. H. Zhao, C. Y. Song, L. C. Wang, *Fuel Cells* 2012, 12, 898.
- [17] A. Zubiaur, M. Chatenet, F. Maillard, S. D. Lambert, J. P. Pirard, N. Job, *Fuel Cells* 2014, 14, 343.
- [18] Z. Zhang, L. Xin, K. Sun, W. Li, *Int. J. Hydrog. Energy* 2011, 36, 12686.
- [19] Y. Zhang, H. Shu, G. Chang, K. Ji, M. Oyama, X. Liu, Y. He, *Electrochim. Acta* 2013, 109, 570.
- [20] G.-J. Chen, J.-S. Wang, F.-Z. Jin, M.-Y. Liu, C.-W. Zhao, Y.-A. Li, Y.-B. Dong, *Inorg. Chem.* 2016, 55, 3058.

- [21] M. Sawangphruk, A. Krittayavathananon, N. Chinwipas, P. Srimuk, T. Vatanatham, S. Limtrakul, J. S. Foord, *Fuel Cells* 2013, 13, 881.
- [22] N. O. Weiss, H. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang, X. Duan, *Adv. Mater.* 2012, 24, 5782.
- [23] Z. Fang, Y. Wang, Z. Liu, A. Schlather, P. M. Ajayan, F. H. L. Koppens, P. Nordlander, N. J. Halas, *ACS Nano* 2012, 6, 10222.
- [24] C.-B. Ma, X. Qi, B. Chen, S. Bao, Z. Yin, X.-J. Wu, Z. Luo, J. Wei, H.-L. Zhang, H. Zhang, *Nanoscale* 2014, 6, 5624.
- [25] C. L. He, Y. X. Jiang, L. Rao, Q. Wang, B. W. Zhang, Y. Y. Li, S. G. Sun, *Fuel Cells* 2013, 13, 873.
- [26] M. Wu, Q. Tang, F. Dong, Y. Wang, D. Li, Q. Guo, Y. Liu, J. Qiao, *Phys. Chem. Chem. Phys.* 2016, 18, 18665.
- [27] X. Zhou, S. Tang, Y. Yin, S. Sun, J. Qiao, *Appl. Energy* 2016, 175, 459.
- [28] F. Cao, M. Zhao, Y. Yu, B. Chen, Y. Huang, J. Yang, X. Cao, Q. Lu, X. Zhang, Z. Zhang, C. Tan, H. Zhang, *J. Am. Chem. Soc.* 2016, 138, 6924.
- [29] B. P. Vinayan, R. Nagar, S. Ramaprabhu, *J. Mater. Chem. A* 2013, 1, 11192.
- [30] J. Y. Kim, N.-J. Choi, H. J. Park, J. Kim, D.-S. Lee, H. Song, *J. Phys. Chem. C* 2014, 118, 25994.
- [31] X. Zhang, J. Zhu, C. S. Tiwary, Z. Ma, H. Huang, J. Zhang, Z. Lu, W. Huang, Y. Wu, *ACS Appl. Mater. Interfaces* 2016, 8, 10858.
- [32] W. Ai, Z. Luo, J. Jiang, J. Zhu, Z. Du, Z. Fan, L. Xie, H. Zhang, W. Huang, T. Yu, *Adv. Mater.* 2014, 26, 6186.
- [33] J. Xu, G. Dong, C. Jin, M. Huang, L. Guan, *ChemSusChem* 2013, 6, 493.
- [34] Y. Zhao, X. Yang, J. Tian, *Electrochim. Acta* 2009, 54, 7114.
- [35] Y. Zhao, X. Yang, J. Tian, F. Wang, L. Zhan, *J. Power Sources* 2010, 195, 4634.
- [36] P. Liu, G. Li, W.-T. Chang, M.-Y. Wu, Y.-X. Li, J. Wang, *RSC Adv.* 2015, 5, 72785.
- [37] Y. Zhao, X. Yang, J. Tian, F. Wang, L. Zhan, *Mater. Sci. Eng. B* 2010, 171, 109.
- [38] B. G. Abraham, K. K. Maniam, A. Kuniyil, R. Chetty, *Fuel Cells* 2016, 16, 656.
- [39] X. Yang, J. Zheng, M. Zhen, X. Meng, F. Jiang, T. Wang, C. Shu, L. Jiang, C. Wang, *Appl. Catal., B* 2012, 121–122, 57.
- [40] B. P. Vinayan, R. Nagar, N. Rajalakshmi, S. Ramaprabhu, *Adv. Funct. Mater.* 2012, 22, 3519.
- [41] S. Yang, L. Zhi, K. Tang, X. Feng, J. Maier, K. M. Ilen, *Adv. Funct. Mater.* 2012, 22, 3634.
- [42] W. Si, J. Zhou, S. Zhang, S. Li, W. Xing, S. Zhuo, *Electrochim. Acta* 2013, 107, 397.
- [43] X. Du, D. Jiang, Q. Liu, J. Qian, H. Mao, K. Wang, *Talanta* 2015, 132, 146.
- [44] Y. Su, Y. Zhang, X. Zhuang, S. Li, D. Wu, F. Zhang, X. Feng, *Carbon* 2013, 62, 296.
- [45] T. Shobha, C. L. Aravinda, P. Bera, L. G. Devi, S. M. Mayanna, *Mater. Chem. Phys.* 2003, 80, 656.
- [46] X. Yang, M. Zhen, G. Li, X. Liu, X. Wang, C. Shu, L. Jiang, C. Wang, *J. Mater. Chem. A* 2013, 1, 8105.
- [47] I. G. Casella, M. Contursi, *Electrochim. Acta* 2006, 52, 649.
- [48] K. Kakaei, M. Dorraji, *Electrochim. Acta* 2014, 143, 207.
- [49] T. Chierchie, C. Mayer, W. J. Lorenz, *J. Electroanal. Chem. Interfacial Electrochem.* 1982, 135, 211.
- [50] Y. Zhao, S. Nie, H. Wang, J. Tian, Z. Ning, X. Li, *J. Power Sources* 2012, 218, 320.
- [51] S. K. Meher, G. R. Rao, *ACS Catal.* 2012, 2, 2795.
- [52] Q. Cui, S. Chao, Z. Bai, H. Yan, K. Wang, L. Yang, *Electrochim. Acta* 2014, 132, 31.
- [53] J. Liu, J. Ye, C. Xu, S. P. Jiang, Y. Tong, *Electrochem. Commun.* 2007, 9, 2334.
- [54] N. Li, Y.-X. Zeng, S. Chen, C.-W. Xu, P.-K. Shen, *Int. J. Hydrog. Energy* 2014, 39, 16015.
- [55] X. Fang, L. Wang, P. K. Shen, G. Cui, C. Bianchini, *J. Power Sources* 2010, 195, 1375.
- [56] P. Jayaweera, S. Hettiarachchi, H. Ocken, *Colloid Surf. A-Physicochem. Eng.* 1994, 85, 19.
- [57] Z. S. Yang, J. J. Wu, *Fuel Cells* 2012, 12, 420.
- [58] Z. X. Liang, T. S. Zhao, J. B. Xu, L. D. Zhu, *Electrochim. Acta* 2009, 54, 2203.