Carbon nanodots prepared from NaOH-boiled graphene and its usage as a support of PdO for ethanol oxidation reaction

Keqiang Ding\textsuperscript{a,b,*}, Pingyuan Wang\textsuperscript{a}, Jing Zhao\textsuperscript{b}, Yuan Li\textsuperscript{b}, Yuying Chen\textsuperscript{b}, Yan Zhang\textsuperscript{b}, Binjuan Wei\textsuperscript{b}, Yanzhi Sun\textsuperscript{a}, Junqing Pan\textsuperscript{a,**}

\textsuperscript{a} State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, China
\textsuperscript{b} College of Chemistry and Materials Science, Hebei Normal University, Shijiazhuang, 050024, China

\section*{Article info}

Article history:
Received 10 November 2016
Received in revised form
1 January 2017
Accepted 30 January 2017
Available online 21 February 2017

Keywords:
Carbon nanodots
Boiling treatment
Graphene
Ethanol oxidation reaction
Electrochemical techniques

\section*{Abstract}

For the first time, carbon nanodots were prepared from NaOH-boiled graphene. And, a novel catalyst that contained PdO and carbon nanodots (denoted as PdO/CND) was fabricated in this work. In this work, 0.5 M and 1.5 M NaOH solutions were respectively employed with an intention to study the influence of NaOH concentration on the electrocatalytic activity of the obtained catalysts for ethanol oxidation reaction (EOR). The obtained samples were thoroughly characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM) and fourier transform infrared spectrometry (FTIR). The results indicated that the intensities of the diffraction peaks for graphene were significantly promoted with increasing the NaOH concentration and carbon nanodots with an average particle size less than 4 nm were fabricated by this developed boiling–grinding–ultrasonication (BGU) method. The electrocatalytic performances of the obtained PdO/CND catalysts for EOR were investigated using cyclic voltammetry (CV) and chronoamperometry (CA). And the consequences strongly demonstrated that PdO/CND prepared from 0.5 M NaOH-boiled graphene showed the best electrocatalytic activity towards EOR among all the prepared catalysts. Developing a very facile method for producing carbon nanodots as well as a novel composite catalyst that contained PdO and carbon nanodots for EOR was the main contribution of this work.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

\section*{Introduction}

Recently, direct ethanol fuel cells (DEFCs), one of the most prospective sources, have attracted giant research interest mainly owing to their superior properties such as the lower toxicity of ethanol, ease production of ethanol, higher theoretical energy density of ethanol (8.01 kWh kg\textsuperscript{-1}) compared to that of methanol (6.09 kWh kg\textsuperscript{-1}) [1]. Therefore, anodic catalyst, on which the process of EOR can proceed very well, was a very crucial factor that could directly influence the further applications of DEFCs. Till present, Pt and Pt-based catalysts have been thought as the best electrocatalysts for EOR because of their satisfactory electrocatalytic activities [2].
However, of late, it was claimed that Pt-based catalysts could be easily poisoned by the CO like intermediates and the kinetics of ethanol electro-oxidation on Pt-based catalysts is quite slow in acidic solution [3]. Also, the higher cost and the limited resources of Pt also greatly restricted the further utilization of DEFCs. Hence, developing novel electrocatalysts with low cost and highly improved kinetics of EOR became into a hot topic in the DEFCs-related research field [4].

Fortunately, recent laborious research works have demonstrated that as an alternative catalyst to Pt, the metal of Palladium (Pd) could exhibit higher electrocatalytic activity and better stability for EOR especially in alkaline media [5]. More importantly, the reserves of Pd are much higher than that of Pt, which could remarkably reduce the catalyst cost. Therefore, exploiting Pd or Pd-based composite catalysts has been very attractive particularly in the electrochemical research area [6].

Recently, the critical role of PdO in improving the electrocatalysis of the Pd-based catalysts has been paid much more attention. For example, Xing's group [7], through annealing the commercial Pd/C catalyst under the O₂ environment, produced a novel Pd-based catalyst, and reported that the produced catalysts exhibited excellent catalytic activity and stability in terms of formic acid electro-oxidation (FAEO), and they deemed that the formed Pd oxides/hydrous oxides (POHOs) could provide the required oxygen species for intermediate CO oxidation during the oxidation process of formic acid. Fan's group [8] also probed the electrocatalytic activity of Pt nanoparticles for methanol oxidation reaction (MOR), in which Pt nanoparticles were electrodeposited on the PdO thin film, and they claimed that the resulting Pt/PdO electrode had a high electrocatalytic activity towards MOR, and they deduced that the synergy of the bifunctional mechanism and the electronic effect should be responsible for the outstanding electrochemical behavior of the prepared Pt/PdO catalyst. In our former work [9], the unexpected role of PdO in improving the electrocatalytic activity of PtₓPdᵧ/MWCNTs towards EOR was also addressed. Although many papers concerning PdO were published every year, as far as we know, no paper reporting the electrocatalytic activity of PdO supported on carbon nanodots towards EOR was published so far.

Meanwhile, very recently, many researchers have emphasized that the properties of the support materials played an important part in augmenting the electrocatalytic activity of a catalyst. Therefore, various kinds of novel support materials were also developed with an intention to enhance the catalytic activity of the Pd-based catalysts. For example, Ni nanowire arrays supported three-dimensional flower-like Pd nano-electrocatalyst was prepared by Razeef's group [10]. Fan and his co-workers [11] reported the preparation of SnO₂ nanospheres supported Pd catalyst. Although, as mentioned above, many novel kinds of support materials were created, the materials of carbon, mainly including carbon black, graphite, carbon nanotubes [12], carbon nanofibers [13] and graphene [14], were still the main Pd catalyst support materials mainly because of their unique merits such as the high electrical conductivity, high surface areas, low cost and simple fabrication process.

Among the widely used support materials of carbon, graphene, as a two-dimensional carbon material, has received increasing attention since its emergence in 2004 [15], mainly owing to its advantageous properties like the high surface area (theoretical specific surface area: 2600 m² g⁻¹), the high carrier mobility, satisfactory thermal conductivity and electric conductivity [16]. To extend the applications of graphene, many strategies have been proposed to modify graphene for its further commercialization. Summari ly, (1) Oxidizing graphene to generate graphene oxide (GO) by a hummer method [17]. Thus, many oxygen-containing groups like hydroxyls, epoxides and carboxyls may grow on the surface of graphene. For instance, Khan's group [18] described the preparation process of GO, and in their works, the concentrated H₂SO₄ and KMnO₄ were employed as the oxidizing agents. (2) Reducing GO to prepare reduced graphene oxide (RGO) [19,20]. It was reported that RGO has rich stacking π electrons, which could facilitate the chemical functionalization with the conjugated molecules through aromatic π−π interactions. (3) Introducing heteroatoms into graphene to produce heteroatom-doped graphene. These heteroatoms mainly included N, P, S and B [21,22]. Nevertheless, to our knowledge, till present, few papers reporting the treatment of graphene via the boiled NaOH solution were published [23].

Very recently, a novel kind of carbon material of carbon nanodots (C-dots, or CND), defined as carbon nanoparticles with sizes below 10 nm, has received enormous interest mainly because of their unique properties [24] like the intense photoluminescence, low toxicity and excellent biocompatibility [25]. Therefore, the research topic of developing novel methods to produce CND has been very attractive in the carbon nanoparticles-related research field. As reported in the previous papers [26], CND, in general, could be fabricated by using two typical methods, i.e., the so-called top—down and bottom—up procedures. As far as we know, the preparation of CND, from graphene via a NaOH-boiling treatment followed by grinding and ultrasonication process, was not reported so far.

In this work, graphene was first boiled in NaOH solution for 2 h to prepare the NaOH-boiled graphene. And then PdO was ground with the boiled graphene for 15 min. Lastly, the generated slurry was ultrasonicated for 6 h, producing PdO/CND composites. The obtained samples were thoroughly featured by XRD, TEM and FTIR measurements. The results of electrocatalytic experiments indicated that the catalyst prepared from 0.5 M NaOH-boiled graphene exhibited the best electrocatalytic performance among all prepared catalysts based on the results of cyclic voltammetry (CV) and chronoamperometry (CA). To our knowledge, this is the first time to report the preparation of carbon nanodots from graphene as well as the production of PdO/CND composite catalysts, which is very beneficial not only to the development of catalyst for EOR but also to the research work of carbon nanodots.

**Experimental**

**Reagents and materials**

Graphene was bought from Fengfan Co., Ltd (China). All electrodes were purchased from Tianjin Aida Co., Ltd (China).
All analytical grade chemicals were received and used without further treatment. Deionized water was used to prepare the aqueous solutions.

**Preparation of PdO/CND**

Firstly, 0.5 g graphene was dispersed in 100 mL NaOH solution (0.5 M and 1.5 M, respectively), and then the suspension solution was boiled for 2 h. To keep the concentration of NaOH identical, a proper amount of distilled water was added during the boiling process. And then, after the solution cooled down to the room temperature naturally, the products were filtered and washed with copious distilled water until the pH value of the filtrate was close to 7. The obtained products were dried under air conditions for 12 h. For comparison, graphene was also boiled in pure distilled water using the same process.

Secondly, 4 mg PdO was mixed with 1 mg of above dried graphene to form a mixture, and then 1 mL distilled water was added into above mixture generating a slurry-like mixture. Subsequently, the resulting mixture was thoroughly ground in an agate mortar for 15 min. Soon afterward, the slurry was transferred into a glass bottle that contained 4 mL distilled water, which was ultrasonicated for 6 h. At last, the products were filtered and dried in air to fabricate the final samples. The samples prepared from distilled water-boiled, 0.5 M NaOH-boiled and 1.5 M NaOH boiled graphene were labeled as PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M, respectively.

**Preparation of PdO/CND modified GC electrode**

1 mg of the resultant sample was dispersed in 1 mL of 0.1 wt.% Nafion ethanol solution, followed by 30 min sonication, generating a catalyst ink. A glassy carbon (GC) electrode (diameter was 3 mm) was polished with 0.05 μm alumina slurry and washed with distilled water. And then 20 μL of above catalyst ink was coated on the well treated GC electrode, and after slow drying in ambient conditions, the PdO/CND modified GC electrodes were produced. The loading of samples on one GC electrode was estimated to be about 1.55 mg cm⁻². And the loading of PdO was approximately close to 0.27 mg cm⁻². Evidently, most of PdO particles were washed off during the preparation process. The electrodes coated with sample PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M were named as electrode a, b and c, respectively.

**Characterization**

The crystallinity and the morphology of the prepared samples were examined by using XRD (Bruker D8 ADVANCE X-ray diffractometer with a Cu Kα source) and transmission electron microscopy (HITACHI, TEM H-7650), respectively. Energy Dispersive X-ray Spectroscopy (EDX) spectrum analysis and Fourier transform infrared spectrometry (FTIR) measurements were performed on an X-ray energy instrument (EDAX, PV-9900, USA) and a Hitachi FT-IR-8900 spectrometer (Japan), respectively. X-ray photoelectron spectroscopy (XPS, Kratos Analytical spectrometer, Al Kα, radiation) were employed to characterize the chemical composition of the prepared catalysts. Room Temperature Raman spectra were recorded using a Renishaw InVia Micro-Raman Spectroscopy System with an excitation wavelength of 514 nm. Electrochemical measurements mainly including CV and CA were carried out on a CHI 660B electrochemical workstation (Shanghai Chenhua Apparatus, China) connected to a personal computer.

In the electrochemical experiment, a traditional three-electrode container was employed, in which PdO/CND modified GC electrode, a saturated calomel electrode (SCE) and a platinum wire served as the working electrode, reference electrode and counter electrode, respectively. All potentials in this paper are reported with respect to SCE. A solution of 1M ethanol in 1M KOH was used to study the electrocatalytic activity of the PdO/CND catalysts for ethanol oxidation reaction (EOR). All the experiments were carried out at room temperature.

**Results and discussion**

**Physical characterization of the prepared PdO/CND**

To examine the structure and crystallinity of prepared PdO/CND, XRD analysis was conducted first and the results are shown in Fig. 1. For the precursor of graphene (pattern o), only a small diffraction peak was observed at 26.7°, indicating that the crystal structure of graphene was identical to that of graphite [27]. Apparently, after the boiling treatment, no novel diffraction peak was observed in the whole diffraction angle range for all the prepared samples. To one’s surprise, no diffraction peaks of metallic Pd or PdO were observed, though the existence of PdO in the samples was verified by the XPS analysis in the subsequent discussion part. This result could only be interpreted as follows [28]: (1) The amount of Pd-based materials was too small to be detected by the XRD analysis. (2) The produced Pd-based materials were amorphous in nature.

Raman spectroscopy is a powerful nondestructive technique which can distinguish the ordered and disordered crystal structures of carbon materials conveniently [29]. Fig. 2 gives the Raman spectra of all the prepared samples. For the pure graphene (curve o), only a weak band positioned at

![Fig. 1 – XRD patterns of the as-prepared samples. Pattern a, b and c correspond to sample PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M. Pattern o corresponds to the graphene.](image-url)
650 cm\(^{-1}\) was displayed. While, for other three samples, three bands, centered at 1355, 1583 and 2729 cm\(^{-1}\), respectively, are exhibited clearly. According to the previous report, the band at about 2729 cm\(^{-1}\) was commonly assigned to the 2D band of graphene, being closely related to the layer thickness of graphene in the sample\[30\]. Generally, the D peak of at around 1355 cm\(^{-1}\) arises from the sp\(^3\) defect sites, while the G peak of 1583 cm\(^{-1}\) is associated with the bond stretching of all sp\(^2\) carbon domains\[31\]. Hence, the intensity ratio of the D and G peaks (ID/IG) can clearly reflect the defect level in graphene. The ratios of ID/IG for sample PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M were 0.091, 0.064 and 1.110, respectively. This result implied that the boiling treatment could alter the defect level of graphene and the sample PdO/CND-0.5M had the most amounts of sp\(^2\) defect sites.

To uncover the functional groups at the surface of the samples, Fourier transform infrared (FTIR) spectra of all samples are compared in Fig. 3. For the pristine graphene, except for the band of at around 3455 cm\(^{-1}\), almost no discernible bands were found. The band at 3455 cm\(^{-1}\) was, commonly, originated from the stretching vibration absorbance of the O–H band. Interestingly, after the NaOH-boiling treatment, some weak bands were clearly observed in the FTIR spectra, indicating that some chemical groups were produced on the surface of graphene. According to the previous work of PdO, these two strong peaks appearing at 337.1 eV and 342.4 eV should be assigned to 3d\(5/2\) and 3d\(3/2\) of PdO, respectively\[35\]. While for sample PdO/CND-0.5M, the Pd 3d peaks, respectively, shifted positively by 0.6 eV and 0.7 eV as compared with those of the pristine PdO. That is to say, after the total preparation process, the electronic state of Pd atom was altered though the valence of Pd element was not changed. This result strongly testified that the element of Pd in all the prepared samples still existed in the form of palladium oxide, and no metallic Pd was produced in the final products, being consistent with that of EDX analysis.

To study the chemical state changes of carbon, XPS spectra of C element for these three samples (graphene, PdO/CND-0M and PdO/CND-0.5M) were presented in Fig. 4b. Based on the prior report, the peak at 284.7 eV should be ascribed to the C1s peak of sp\(^2\) hybridized carbon (sp\(^2\)-C)\[36\]. Apparently, the peak intensity for C1s was significantly increased after the NaOH-boiling treatment, which indicated that more sp\(^2\) hybridized carbons were fabricated in sample PdO/CND-0.5M. Thus, it can be concluded that compared to the water boiling treatment, NaOH solution boiling treatment could greatly enhance the amounts of sp\(^2\) hybridized carbons in the

---

**Fig. 2 – Raman spectra of the as-prepared samples.** Pattern a, b and c correspond to sample PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M. Curve o corresponds to the graphene.

**Fig. 3 – FTIR spectra of synthesized samples.** Curves a, b and c correspond to sample PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M. Curve o corresponds to the pure graphene.
Obviously, more sp² hybridized carbons were contained in the sample of PdO/CND-0.5M, which was in agreement with the results of Raman spectroscopy (Fig. 2). TEM images of these three samples (PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M) are displayed in Fig. 5. To one's surprise, very small and uniform carbon particles were produced via this developed boiling–grinding–ultrasonication (BGU) method. Meanwhile, no obvious agglomeration of these nanoparticles was found in terms of sample PdO/CND-0.5M and PdO/CND-1.5M. The particle size ranges for sample PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M were estimated to be approximately 2.2–4.5 nm, 1.8–3.9 nm and 3.8–8.2 nm, respectively, based on the rough particle size estimation from randomly selected 200 particles. According to the definition of carbon nanodots, the particles prepared here should be nominated as carbon nanodots (CND). Si's group [25] synthesized C-dots through femtosecond laser ablation of graphite powder in a polyethylene glycol solution, in his work, the mean size of the prepared carbon nanodots was approximately 1.5 nm. Balzaretti and his co-workers [27] prepared carbon nanodots via a pyrolysis of methyl groups well dispersed on the edges of nanometric grains of silica previously cold sintered under high pressure. In their works, the average size of the carbon particles was estimated to be 6.8 nm. However, in their works, the size distribution of the prepared carbon particles was not uniform. Therefore, the BGU method developed here for producing carbon nanodots was a novel method, and the physical properties of our prepared carbon nanodots were comparable to those of previously prepared C-dots in terms of particle size and size distribution. Also, the method we developed here was rather simple as compared to the published methods of fabricating C-dots.

According to the above characterizations, probably, it can be inferred that after the boiling treatment, many –OH groups were formed on the surface of graphene, thus, the pure graphene with only C=C bonds was converted into the boiled graphene with many–OH groups. As a result, an inhomogeneous distribution of chemical bonds was generated in the NaOH-boiled graphene. And in the grinding process, many chemical bonds were destroyed by the stress from grinding, leading to the formation of numerous eyelets on the surface of graphene [37]. And then, in the ultrasonication treatment, the graphene with eyelets were divided into many nanodots to reach a new energy state. Finally, carbon nanodots were produced by this boiling–grinding–ultrasonication (BGU) method successfully.
Electrocatalytic performances of the PdO/CND catalysts

The electrocatalytic activities of the prepared samples for EOR were firstly investigated by using cyclic voltammetry (CV), and the cyclic voltammograms (CVs) measured in 1M KOH containing 1M ethanol are shown in Fig. 6. Apparently, two characteristic oxidation peaks of EOR were displayed on all the PdO/CND coated GC electrodes, which explicitly documented that this developed novel composite having PdO and CND had evident electrocatalytic activities towards EOR. The peak potentials and onset potentials of the positive potential-direction oxidation peak for sample PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M were estimated to be −0.29 V and −0.61 V, −0.31 V and −0.64 V, −0.28 V and −0.55 V, respectively. It indicated that the over potential of EOR on the catalyst PdO/CND-0.5M was smaller as compared to those of catalyst PdO/CND-0M and PdO/CND-1.5M. Careful inspection revealed that these well-defined electro-oxidation peaks were composed of peak f located at −0.30 V in the anodic sweep and peak b positioned at −0.39 V in the cathodic sweep, which was consistent with the previous report [23] very well. Ordinarily, the forward oxidation peak f is resulted from the oxidation of freshly chemisorbed species (which came from ethanol adsorption), and the reverse oxidation peak b is primarily related to the electro-oxidation of carbonaceous species which were not completely oxidized in the forward scan [38]. And, the ratio of the peak current of peak f to that of peak b, i.e., If/Ib, could generally be reckoned as a parameter to evaluate the poisoning tolerance of a catalyst [39]. A larger If/Ib ratio value, generally, indicates a better oxidation ability of ethanol during the anodic potential sweep. The ratios of If/Ib for catalyst PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M were calculated to be 0.60, 0.68 and 0.77, respectively. Although the largest value of If/Ib was exhibited by catalyst PdO/CND-1.5M, the peak current of PdO/CND-1.5M was too small to be employed as a catalyst for EOR. Therefore, catalyst PdO/CND-0.5M, due to its largest peak current, had the best electrocatalytic activity for EOR among all prepared catalysts. This result probably was resulted from the following reasons: (1) The crystallinity of the CND in sample PdO/CND-0.5M was higher than that of sample PdO/CND-0M, which was beneficial to the “directional transferring of electrons”; (2) The particle size of CND for sample PdO/CND-0.5M was relatively smaller when compared to other samples, which may provide a larger contact area between the electrode and electrolyte when the loadings were identical. As a result, the values of over potential for EOR could be greatly reduced according to the Tafel equation [40]; (3) Larger amounts of sp² defect sites and −OH groups in the CND of sample PdO/CND-0.5M probably reinforced the interaction between carbon support and PdO particles, which could remarkably promote the electrocatalysis of PdO towards EOR.

To probe the service life of the PdO/CND catalysts in the EOR, Chronoamperometric (CA) measurements were also performed in a 1M KOH solution having 1M ethanol. Fig. 7 shows the relationship between the polarized currents and testing period, which was recorded at the potential of −0.24 V versus SCE. Curves a, b and c correspond to sample PdO/CND-0M, PdO/CND-0.5M and PdO/CND-1.5M.
and 1.8 mA cm\(^{-2}\) at 600 s, respectively. This result substantially certified that catalyst PdO/CND-0.5M exhibited not only the largest polarized current density but also the best durability and stability among all the synthesized catalysts, being consistent with the CV results (Fig. 6).

**Analyzing the possible electrocatalytic mechanism**

To further investigate the reasons why above three kinds of PdO/CND catalysts exhibited such different electrocatalytic activities towards EOR, CVs of these three catalysts in 1M KOH are plotted in Fig. 8. Apparently, the shapes of these CV curves were very similar to that of pure Pd electrode in KOH solution. Thus, the reduction peaks appearing at \(-0.44\) V should correspond to the electrochemical reduction of PdO [42]. Thus, basing on the comparison between Fig. 8 and Fig. 6, it can be concluded that prior to the electro-oxidation of ethanol, PdO has been electrochemically reduced to be metallic Pd [43,44]. As a result, EOR could proceed well on the newly-produced metallic Pd, showing similar CV curves of EOR to that on the Pd surface. That is to say, EOR still proceeded on the Pd surface rather than the surface of PdO. Meanwhile, according to the previous report [4], the electrochemically active surface area (EASA) of a Pd-based electrode could be estimated from the peak area of the PdO reduction peak. Apparently, sample PdO/CND-0.5M had the smallest value of EASA among all the samples based on a rough estimation, which was very opposite to the previous result that larger value of EASA corresponded to a better electrocatalytic activity of an electrocatalyst. Therefore, probably, there was a synergistic reaction between PdO and the newly-prepared metallic Pd, which led to the significantly increased electrocatalytic activity towards EOR [9].

Although the exact electro-oxidation mechanism of EOR remained unclear, the widely accepted mechanism of EOR has been proposed previously as shown below [45].

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow (\text{CH}_3\text{CH}_2\text{OH})_{\text{ads}} \quad (1)
\]

\[
(\text{CH}_3\text{CH}_2\text{OH})_{\text{ads}} + 3\text{OH}^- \rightarrow \text{CH}_3\text{CO}_{\text{ads}} + 3\text{H}_2\text{O} + 3\text{e}^- \quad (2)
\]

\[
\text{OH}^- \leftrightarrow \text{OH}_{\text{ads}} + \text{e}^- \quad (3)
\]

\[
\text{CH}_3\text{CO}_{\text{ads}} + \text{OH}_{\text{ads}} \rightarrow \text{CH}_3\text{COOH} \quad (4)
\]

\[
\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \quad (5)
\]

Basing on above steps, the presence of large amounts of OH\(^-\) would be favorable to step 2, which could yield a larger amount of OH\(_{\text{ads}}\). The produced OH\(_{\text{ads}}\) groups would accelerate the step 4 and 5. As discussed in the part concerning Fig. 3, more \(-\text{OH}\) groups were contained in sample PdO/CND-0.5M, consequently, the electrocatalytic activity of catalyst PdO/CND-0.5M towards EOR was significantly promoted, leading to an enhanced peak current of EOR. To our knowledge, this is the first time to report the fact that PdO supported on carbon nanodots could be utilized as electrocatalysts for EOR.

**Conclusion**

For the first time, PdO supported carbon nanodots composite catalysts (PdO/CND) were prepared by a facile BGU method. XRD result revealed that the NaOH-boiling treatment could greatly increase the crystallinity of the used graphene. TEM images indicated that carbon nanodots with an average size less than 4 nm were prepared from graphene. The results from electrochemical measurement, also, demonstrated that the composite containing PdO and 0.5M NaOH-boiled graphene delivered the best electrocatalytic activity towards EOR among all the prepared samples. Developing a novel method to prepare carbon nanodots as well as to produce a novel catalyst denoted as PdO/CND was the main contribution of this work, which was very favorable to the development of novel electrocatalysts for EOR.

**Acknowledgements**

This work was financially supported by National Natural Science Foundation of China (No. 21676022 & 21173066), the State Key Program of National Natural Science of China (21236003), Natural Science Foundation of Hebei Province of China (No. B2011205014 and B2015205150), the Fundamental Research Funds for the Central Universities (JD1612 and YS1406), BUCT Fund for Disciplines Construction and Development (No. XK1533).

**REFERENCES**

[1] Li M, Cullen DA, Sasaki K, Marinkovic NS, More K, Adzic RR. Ternary electrocatalysts for oxidizing ethanol to carbon


