A two step method to synthesize palladium–copper nanoparticles on reduced graphene oxide and their extremely high electrocatalytic activity for the electrooxidation of methanol and ethanol

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Highlights
• A two step method for the preparation of Pd–Cu/RGO hybrids containing different amounts of Cu.
• After the two step reaction, the catalysts form a bimetallic structure of a small Pd–Cu core and a thin Pd rich shell.
• The samples have better catalytic property for alcohol electrocatalytic oxidation than many other Pd-based catalysts.

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Abstract
Palladium–copper nanoparticles (Pd–Cu NPs) supported on reduced graphene oxide (RGO) with different Pd/Cu ratios (Pd–Cu/RGO) were prepared by a two step method. The Pd–Cu/RGO hybrids were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction and thermogravimetric analyses. Cyclic voltammetry and chronoamperometry were used to investigate the electrochemical activities and stabilities of the Pd–Cu/RGO catalysts for the electro-oxidation of methanol and ethanol in alkaline media. The Pd–Cu/RGO catalysts exhibited high catalytic activities and good stabilities. This is because the catalysts have a bimetallic structure consisting of a small Pd–Cu core surrounded by a thin Pd-rich shell which improves the catalytic activities of the Pd–Cu/RGO hybrids. Thus they should be useful in direct methanol and ethanol fuel cells.

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1. Introduction
A fuel cell is an electrochemical engine that can convert the free energy change of a chemical reaction directly into electrical energy [1]. Since direct alcohol fuel cells (DAFCs) are highly efficient power generators and have good environmental performance, they are considered to be the best choice for clean and efficient power generators and so they have attracted a great deal of attention from researchers, companies and governments [2]. Alcohols, like methanol and ethanol, are the most promising candidates for DAFCs since they are easily handled, transported and stored, and they have high theoretical energy densities [3].

DAFCs have been extensively studied, but they still have many problems including a shortage of appropriate anodic catalysts and low catalytic activities. Studies have shown that Pt-based catalysts are promising catalysts since they have the highest catalytic activities among the anode electrocatalysts for methanol and ethanol oxidation [4]. However, Pt and Pt-based catalysts have some disadvantages like their high costs due to the limited supply of Pt. To solve this problem, palladium (Pd) has emerged as an attractive replacement for Pt-based catalysts in fuel cells. Compared to Pt, Pd has a lower price, a higher abundance and better electrocatalytic activity and it is especially effective in alkaline environments [5].

A great deal of effort has been made to improve the catalytic efficiency of Pd catalysts for methanol and ethanol oxidations. One approach is to control the size and morphology of the Pd nanostructures. A variety of chemical protocols have been developed for achieving partial control of nanostructures. For instance, nanoparticles, nanocubes, nanoflowers, nanowires, nanotubes, and...
nanoporous (or mesoporous) and dendrite structures have all been fabricated [6–13]. Among these, Pd nanoparticles are of particular interest in catalysis due to their high surface areas and good catalytic activities.

Alloying Pd with a second metal (M = Co, Ni, or Sn) is also a way to reduce the Pd dosage and to enhance catalytic performance [14–17]. However, catalysis at the electrode of a fuel cell is a surface phenomenon and the catalytic activity of Pd depends on the dispersion or exposed percentage of Pd atoms in the catalyst [18]. Therefore, the design of hybrids which contains more Pd at the outer surface of the material is being pursued in order to make the most efficient use of the Pd metal. This is a promising way to enhance the catalytic performance. This new class of catalysts can significantly enhance the kinetics of methanol and ethanol oxidation reactions, and at the same time these catalysts possess improved Pd stability under typical fuel cell operating conditions [19].

Another way to enhance the activity of noble metals nanocatalysts and to lower the usage of it is to load the nanocatalyst onto the surface of a suitable support material [20]. Carbon materials are inexpensive and have large surface areas and good electrical conductivities. So they are ideal support materials for nanoparticle catalysts. Carbon black and carbon nanotubes have been used as support materials for dispersing and stabilizing Pd-based catalysts [21–25], Graphene, a sp²-hybridized two dimensional mono-layer carbon sheet, has become a popular support material for nanoparticles because of its superior thermal and electric conductivities, high chemical stability, broad electrochemical window and unique graphitized basal plane structure [26–29]. Many monometallic and bimetallic nanoparticles, such as Pd [30], Au [31], Pt–Cu [32], Pd–Ag [33] and Au–Pd [34] have been dispersed on graphene, and these materials have shown impressive catalytic behaviors for various reactions.

In this paper, Pd–Cu bimetallic hybrids supported on reduced graphene oxide (RGO) were investigated for the oxidation of methanol and ethanol. Herein a two-step method for the preparation of Pd–Cu/RGO hybrids which contain different amounts of Cu is presented. Sodium citrate was used as an ecofriendly reducing agent to reduce H2PdCl4, CuSO4 and GO in one pot with the subsequent galvanic displacement reaction between first step sample and PdCl2 in aqueous solution [35]. Due to the modification of the structure and composition, we anticipate the catalytic activities can be quite different from those of the pure metals Pd NPs. The catalytic activity of these Pd–Cu/RGO hybrids for the electro-oxidation of methanol and ethanol was studied.

2. Experimental details

2.1. Materials

Natural graphite powder was purchased from Qingdao Graphite Factory. Potassium permanganate, sodium nitrate, concentrated sulfuric acid, hydrogen peroxide (30%), hydrochloric acid, ethylene glycol (EG), sodium citrate, potassium palladium (II) chloride (K2PdCl4) and copper sulfate were all from Sigma. All other reagents were purchased from Tianjin Chemical Reagent Company. All reagents were analytical grade and were used as received without any further purification.

2.2. Synthesis of Pd–Cu/RGO hybrids

A modified Hummers’ method was employed to produce graphite oxide from natural graphite powder [36], Pd–Cu/RGO was prepared by a two-step method. In a typical process, 8 mL K2PdCl4 aqueous solution (0.5 mg mL⁻¹), 12 mL CuSO4 aqueous solution (1 mg mL⁻¹) and sodium citrate (120 mg) were dissolved in ethylene glycol (EG) in a flask and stirred for 0.5 h to obtain a homogeneous solution. The solution was then added to 6 mL prepared graphene oxide suspension (4.2 mg mL⁻¹) with stirring and its pH was adjusted to 10 by the dropwise addition of a 5 wt % KOH/EG solution. The mixed solution was heated to 160 °C and maintained at this temperature for 6 h. The resultant precipitate was collected by filtration and then washed three times with deionized water and finally dried in air for 12 h. This resulted in the first step sample designated as Pd–Cu/RGO-1.

The Pd–Cu/RGO-1 was then added to a flask containing only an aqueous solution of K2PdCl4 (11 mL, 0.5 mg mL⁻¹). The mixture was stirred for 4 h at 80 °C and the resultant solid was collected by filtration, washed with deionized water, and dried in air for 12 h. This sample is designated as Pd–Cu/RGO. The weight percent of Pd in the Pd–Cu/RGO was about 10 wt % and the atomic ratio of Pd to Cu was 1:1 (Pd–Cu1:1)/RGO. In order to find which ratio led to the best catalytic activity, Pd–Cu (1:0.8)/RGO, and Pd–Cu (1:1.2)/RGO with the same 10 wt % of Pd were also prepared using the same procedure.

2.3. Characterization

2.3.1. X-ray diffraction analysis

The X-ray diffraction (XRD) spectra of the samples were measured using an X-ray diffractometer (BOD3300) with a reference target: Cu Ka radiation (λ = 1.54 Å), voltage: 30 kV and current: 30 mA. The samples were measured from 30° to 90° (2θ) at steps of 4° min⁻¹.

2.3.2. X-ray photoelectron spectroscopy (XPS) analysis

Elemental analysis was conducted on an X-ray photoelectron spectrometer with a Mg Ka anode (PHI1600 ESCA System, PERKIN ELMER, US).

2.3.3. Thermogravimetric analysis

Prior to thermogravimetric analysis (TGA), the samples were dried in a vacuum at 50 °C for 2 days. TGA was performed with a Rigaku-TD-TDA analyzer with a heating rate of 10 °C/min.

2.3.4. Transmission electron microscopy (TEM) observation

TEM and line profile measurements were performed using a Philips Tecnai G² F20 microscope at 200 kV.

2.4. Electrochemical measurements

The electrochemical measurements, including cyclic voltammetry and chronopotentiometry, were performed with a CHI 660D electrochemical work station (CH Instruments, Inc, Shanghai) at ambient temperature. The counter and reference electrodes were a platinum mesh and a Hg/HgO (1.0 M KOH) electrode, respectively. The working electrode was prepared by dropping 5 μL of catalyst ink onto a glassy carbon electrode (GCE) with a diameter of 3 mm. The ink was prepared by ultrasonically mixing 4 mg of Pd–Cu/RGO with 1.9 mL of ethanol and 0.1 mL of Nafion solution. The electrolyte was 1 M KOH/1 M CH3OH or 1 M KOH/1 M CH3CH2OH, and oxygen was removed from all solutions by purging the electrolyte with an inert gas for 20 min.

3. Results and discussion

The morphology of both the first step sample (Pd–Cu/RGO-1) and second step sample (Pd–Cu/RGO) were observed by TEM. The TEM images of Pd–Cu (1:1)/RGO-1 (Fig. 1a) and Pd–Cu (1:1)/RGO (Fig. 1b) show that the Pd–Cu nanoparticles were well dispersed on the rGO layers and they have a narrow size distribution. The
Fig. 1. TEM images of Pd–Cu (1:1)/RGO-1 (a) and Pd–Cu (1:1)/RGO (b). HRTEM images of Pd–Cu (1:1)/RGO-1 (c) and Pd–Cu (1:1)/RGO (d). The EDX spectra of Pd–Cu (1:1)/RGO-1 (e) and Pd–Cu (1:1)/RGO (f). The EDX line-scans of Pd–Cu (1:1)/RGO-1 (g) and Pd–Cu (1:1)/RGO (h).
nanoparticles are small with sizes of about 10 nm. Typical HRTEM images of Pd\textsubscript{1}Cu\textsubscript{1} (1:1)/RGO-1 (Fig. 1c) and Pd\textsubscript{1}Cu\textsubscript{1} (1:1)/RGO (Fig. 1d) show that the nanoparticles have multi-phase structures which is indicated by the periodic lattice fringes with distinct interplanar spacing. In Pd\textsubscript{1}Cu\textsubscript{1} (1:1)/RGO-1, one of the lattice fringe spacings is 0.224 or 0.223 nm which is consistent with the distance between the dominant (111) face-centered cubic (fcc) planes of Pd\textsuperscript{35}. The other spacing is 0.195 nm which corresponds to the interplanar distance of the (111) planes of fcc-Cu\textsuperscript{37}. The Pd\textsubscript{1}Cu\textsubscript{1} (1:1)/RGO image shows the same result. These results indicate that both the first step sample and the second step sample formed a bimetallic nanoparticles.

The EDX spectra of Pd\textsubscript{1}Cu\textsubscript{1} (1:1)/RGO-1 (Fig. 1e) and Pd\textsubscript{1}Cu\textsubscript{1} (1:1)/RGO (Fig. 1f) indicate that both samples contain Pd and Cu. The weight ratio was calculated by the software of TEM Imaging & Analysis offline. The weight percentages of Cu and Pd are 69.5% and 30.5% in Pd\textsubscript{1}Cu\textsubscript{1} (1:1)/RGO-1 and those in Pd\textsubscript{1}Cu\textsubscript{1} (1:1)/RGO are 41.5% and 58.5%. These data further confirm that both the hybrids formed a bimetallic nanoparticles, and the amount of Pd increased after the second step. There also exist Ni peaks which come from the Ni substrate.

To further understand the changes of the Pd–Cu nanoparticles during the second step, EDX line profiles were performed on nanoparticles from both Pd–Cu (1:1)/RGO-1 and Pd–Cu (1:1)/RGO. The line profile of Pd–Cu (1:1)/RGO-1 (Fig. 1g) shows that the Cu and Pd atoms are evenly distributed throughout the Pd–Cu nanoparticles, although there is more Cu than Pd. Interestingly, the line profile of Pd–Cu (1:1)/RGO (Fig. 1h) shows that after the second step, both the Cu and Pd atoms are still distributed throughout the entire particle but the outer surface has more Pd atoms. The Pd atoms form a rich shell which should be good for improving catalytic activity.

From the TEM data illustrated, the formation process of the Pd–Cu/RGO hybrids is assumed to be a two-step process. In the first step, the following reactions take place:

\[
\text{Cu}^{2+} + 2e = \text{Cu}
\]

\[
\text{PdCl}_4^{2-} + 2e = \text{Pd} + 4\text{Cl}^{-}
\]

In the second step, the Cu NPs are partially replaced by Pd NPs via a redox reaction between Cu and Pd\textsuperscript{2+} ions to form a Pd rich shell structure.

\[
\text{Cu} + \text{Pd}^{2+} = \text{Pd} + \text{Cu}^{2+}
\]

A schematic illustration of these steps are shown in Scheme 1. First, Pd–Cu cores were synthesized on RGO sheets dispersed in an ethylene glycol solution, and then some of the Cu atoms in the outer layer of the Pd–Cu core were sacrificed to reduce PdCl\textsubscript{4}\textsuperscript{2-} to form a Pd rich shell.

Fig. 2 shows the XRD patterns of Pd/RGO (a) and Pd–Cu/RGO NPs prepared with different Pd–Cu ratios (b, c, d) and Pd–Cu (1:1)/RGO-1 (e). For Pd/RGO, the peaks at about 40.0°, 46.4°, 68.0° and 81.9° correspond to the (111), (200), (220) and (311) lattice planes of the face center cubic crystalline structure of Pd, respectively\textsuperscript{38}.
The XRD spectra of the Pd–Au/RGO with different Pd/Cu ratios are similar. These spectra contain a new diffraction peak at $2\theta = 44.50^\circ$, which can be assigned to the (111) reflections of Cu [39]. All the Pd–Cu/RGO hybrids exhibit characteristic diffraction peaks for fcc Pd although the incorporation of Cu caused the Pd peaks to shift to higher angles as the content of Cu increased. These XRD results again demonstrate that Pd–Cu/RGO contains Pd–Cu bimetallic nanoparticles.

XPS analysis was used to determine the surface composition of the Pd–Cu (1:1)/RGO hybrids. Fig. 3 shows the XPS spectra of Pd–Cu (1:1)/RGO-1 (Fig. 3a) and Pd–Cu (1:1)/RGO (Fig. 3b). Both spectra contain a C1s peak at about 284 eV, an O1s peak at about 531 eV, a Pd3d peak at about 340 eV and a Cu2p peak at about 935 eV. This indicates that the Pd–Cu/RGO contains C, O, Pd and Cu. The Pd and Cu are from the bimetallic NPs whereas the C and O are from the RGO.

The high-resolution C1s XPS spectra of Pd–Cu (1:1)/RGO-1 (Fig. 3c), Pd–Cu (1:1)/RGO (Fig. 3d) and GO (Fig. 3e), show that the samples contain alkyl Cs, an sp$^2$-bonded carbon network (C–C/C=C, 284 eV), hydroxyl and epoxy groups (C–O, 286 eV), and carbonyl groups (C=O, 288 eV) [14]. The C–C/O peak intensity ratios in the Pd–Cu (1:1)/RGO-1 and Pd–Cu (1:1)/RGO spectra obviously increased compared to GO which confirms the efficient reduction of GO. The C/O ratios of Pd–Cu (1:1)/RGO-1 and Pd–Cu (1:1)/RGO are 3.31 and 6.03, respectively, which is higher than that of GO (2.30). This indicates that many of the oxygen-containing functional groups were removed during the reduction process, suggesting that GO was reduced.

The XPS Pd3d and Cu2p spectra of Pd–Cu (1:1)/RGO were also collected in order to determine the valence states of the Pd and Cu in the hybrid. The Pd 3d5/2 peak at 337.5 eV and the 3d3/2 peak at 342.8 eV (Fig. 4a) can be attributed to metallic Pd$^0$ which indicates the complete reduction of the Pd precursors [40]. A similar conclusion can be made for Cu, since the Cu 2p region (Fig. 4b)
contains peaks at 934.5 and 954.0 eV (f) which can be ascribed to 2p3/2 and 2p1/2 of Cu [34]. The predominant Pd⁰ and Cu⁰ species are expected to improve the catalytic activity of the hybrid for alcohol oxidation [41].

TGA analysis was conducted on GO (Fig. 5, curve i), Pd–Cu (1:1)/RGO (Fig. 5, curve ii), and Pd–Cu (1:0.8)/RGO (Fig. 5, curve iii). For all samples the weight loss below 100 °C is due to the escape of water molecules adsorbed between the RGO nanosheets. For GO (Fig. 5, curve i), a weight loss of about 30% occurred between 100 and 200 °C. This can be attributed to the removal of some of the oxygen-containing functional groups [42]. The weight loss above 200 °C is due to the removal of the remaining oxygen-containing functional groups [42]. The weight loss in Pd–Cu (1:1)/RGO-1 (Fig. 5, curve ii) below 300 °C is only about 10% of that in GO and that in Pd–Cu (1:1)/RGO (Fig. 5, curve iii) is about 6% of the loss in GO. The total weight loss of Pd–Cu (1:1)/RGO-1 and Pd–Cu (1:1)/RGO are much smaller than GO, which indicates that the GO in Pd–Cu (1:1)/RGO-1 and Pd–Cu (1:1)/RGO were partially reduced after the thermal treatment. These results also in accordance with the XPS results.

The electrocatalytic properties of the Pd–Cu/RGO hybrids for methanol and ethanol oxidation were carried out in KOH solution. KOH was used because the reaction is faster in alkaline solutions [43]. The electrocatalytic activities of Pd/RGO and Cu/RGO were also tested as controls.

First, the background cyclic voltammograms of Pd/RGO (i), Pd–Cu (1:1)/RGO (ii), Pd–Cu (1:1)/RGO-1 (iii), Pd–Cu (1:0.8)/RGO (iv), Pd–Cu (1:1.2)/RGO (v) and Cu/RGO-1 (vi) in 1 M KOH at a scan rate of 50 mV s⁻¹ between −1.0 and 0.6 V were collected (Fig. 6). The electrocatalytic data of Cu/RGO-1 were calculated based on the amount of loaded Cu (mass activity). Except Cu/RGO-1, those of other Pd contained catalysts were calculated based on the amount of loaded Pd (mass activity). For all the catalysts, the peaks for the adsorption/desorption of hydrogen appeared between −0.8 and −0.6 V. The peaks for the oxidation of Pd and the reduction of palladium oxide were around 0.4 V and 0.3 V, respectively [21]. There are no peaks for Cu and its oxide, so it can be inferred that Cu was not active in this system.

The cyclic voltammograms of Pd–Cu (1:1)/RGO (i), Pd–Cu (1:0.8)/RGO (ii), Pd–Cu (1:1.2)/RGO (iii), Pd–Cu (1:1)/RGO-1 (iv), Pd/RGO (v) and Cu/RGO-1 (vi) modified electrodes in 1 M KOH/1 M CH₃OH at a scan rate of 50 mV s⁻¹ are shown in Fig. 7. The peaks in the forward scans correspond to methanol oxidation, whereas the peaks in the backward scans are attributed to the removal of incompletely oxidized CO-like carbonaceous species [44]. The forward anodic peak current densities of these electrodes are listed in Table 1. The current densities increase in the order of Cu/RGO-1 < Pd/RGO < Pd–Cu (1:1)/RGO < Pd–Cu (1:1.2)/RGO < Pd–Cu (1:0.8)/RGO < Pd–Cu (1:1)/RGO. The current density of Pd–Cu (1:1)/RGO (1153.4 mA mg⁻¹ Pd) is higher than those previously reported for other Pd-based catalysts, such as Pd–Co/RGO (320.8 mA mg⁻¹ Pd) and Pd–Ag/RGO (630 mA mg⁻¹ Pd) [15,31].

The onset potential for Pd–Cu (1:1)/RGO was −0.10 V, which is more negative than that for the other catalysts. The Pd–Cu (1:1)/RGO had the highest current density and the most negative shift of the onset potential both of which are very important for good electrocatalytic performance.

The peak current density for the Pd/RGO electrode was 358.5 mA mg⁻¹ Pd, and the peak current densities of the Pd–Cu/RGO electrodes were much higher than that of the Pd/RGO [45]. The exact reason is not clear, but this could be due to the synergistic effects between the Pd and the Cu metals. Alloyed Cu can decrease the electronic binding energy in Pd and facilitate the C–H cleavage reaction at relatively low potentials which improves the electrocatalytic activity for alcohol oxidation [46]. At the same time, a
The catalytic activities of Pd–Cu (1:1) RGO hybrids were all higher than that of Pd–Cu (1:1)/RGO-1. This is because the second step of the preparation process produces Pd shells and so the Pd–Cu/RGO hybrids contain more Pd than Pd–Cu (1:1)/RGO-1. A Pd rich shell on the hybrids surface shows significantly higher electrocatalytic activity than the original hybrids in oxidation of methanol. This is due to catalysis at the electrode of a fuel cell is a surface phenomenon and the exposed amount of Pd increased after the second step. This is also supported by the fact that the catalytic performance of Pd–Au/RGO was greatly improved when fabricated with a Pd-rich shell.

The current densities of the three Pd–Cu/RGO hybrids were all higher than that of Pd–Cu (1:1)/RGO-1. This is because the second step of the preparation process produces Pd shells and so the Pd–Cu/RGO hybrids contain more Pd than Pd–Cu (1:1)/RGO-1. A Pd rich shell on the hybrids surface shows significantly higher electrocatalytic activity than the original hybrids in oxidation of methanol. This is due to catalysis at the electrode of a fuel cell is a surface phenomenon and the exposed amount of Pd increased after the second step. This is also supported by the fact that the catalytic performance of Pd–Au/RGO was greatly improved when fabricated with a Pd-rich shell.

The transportation characteristics of methanol on the Pd–Cu (1:1)/RGO modified electrode were investigated by varying the scan rate in 1 M KOH/1 M CH3OH and the results are shown in Fig. 8. The anodic peak current density increased with increasing scan rate, indicating that the electrocatalytic oxidation of methanol on the Pd–Cu (1:1)/RGO modified electrode may be a diffusion-controlled process. As shown in the insert in Fig. 8, the relationship between the forward scan peak current densities and \( v^{1/2} \) is linear. This indicates that the electrocatalytic oxidation of methanol on Pd–Cu/RGO is in fact a diffusion controlled process.

The catalytic activities of Pd–Cu (1:1)/RGO (i), Pd–Cu (1:0.8)/RGO (ii), Pd–Cu (1:1.2)/RGO (iii), and Pd–Cu (1:0.8)/RGO (iv), for the electro-oxidation of ethanol were also examined (Fig. 9). The peak potentials and peak current densities are listed in Table 2. For the electro-oxidation of ethanol, the Pd–Cu (1:1)/RGO electrode still had the highest peak current density (2112.4 mA mg⁻¹ Pd), indicating that the Pd–Cu (1:1)/RGO electrode is an excellent catalyst for alcohol electro-oxidation.

Chronoamperometry was employed to examine the electrocatalytic stability of the catalysts. Curves for Pd–Cu (1:1)/RGO (Fig. 10, curve a), Pd–Cu (1:1)/RGO-1 (Fig. 10, curve b) and Pd/RGO (Fig. 10, curve c) catalysts modified electrodes were recorded at a potential of 0.30 V in 1 M KOH/1 M CH3OH. In general, all CA curves present a gradual decline in current density. The decline results from poisoning of the electrocatalysts, such as formation of oxides or hydroxides and other poisoning intermediates adsorbed on the electrocatalysts during alcohol electrodeoxidation [50]. In methanol solution, the steady current densities remain about 79 and 106 mA mg⁻¹ on Pd–Cu/RGO-1 and Pd–Cu/RGO, respectively, compared with 17 mA mg⁻¹ on Pd/RGO. It is clearly that the current densities on both the Pd–Cu (1:1)/RGO-1 and Pd–Cu (1:0.8)/RGO catalysts are higher than those on Pd/RGO for all CA measurements. The similar results were obtained in 1 M KOH/1 M CH3OH (Fig. 11). In ethanol solution, the Pd–Cu/RGO catalysts still exhibit excellent stability. These results prove that Pd–Cu/RGO possesses high activity for oxidation of methanol or ethanol and exhibits superior electrochemical catalytic stability.

4. Conclusions

Pd–Cu/RGO hybrids with different Pd/Cu ratios were prepared by a two-step method. After the second step, the Pd–Cu/RGO hybrids exhibited good electrochemical catalytic activity for methanol and ethanol electro-oxidation. Among the catalysts, Pd–Cu (1:1)/RGO...
CH₃CH₂OH solution. size and shape but also on its composition. Therefore the Pd catalyst can indeed be improved through control not only on Pd NP oxidation, respectively. In addition, the Pd fuel cells.

RGO hybrids should be very useful for use in direct methanol and ethanol fuel cells.

Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak potential (V) vs. Hg/HgO</th>
<th>Peak current density (mA mg⁻¹ Pd)</th>
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</thead>
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<tr>
<td>Pd–Cu (1:1)/RGO</td>
<td>0.15</td>
<td>2105.4</td>
</tr>
<tr>
<td>Pd–Cu (1:0.8)/RGO</td>
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<td>1584.8</td>
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<tr>
<td>Pd–Cu (1:1.2)/RGO</td>
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<td>1310.1</td>
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<tr>
<td>Pd–Cu (1:1)/RGO-1</td>
<td>0.18</td>
<td>834.8</td>
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</table>

Fig. 10. Chronoamperometry curves collected for 3000 s at 0.3 V for Pd–Cu (1:1)/RGO (a), Pd–Cu (1:1)/RGO-1 (b) and Pd/RGO (c) modified electrodes in 1 M KOH/1 M CH₃OH solution.

Fig. 11. Chronoamperometry curves collected for 3000 s at 0.3 V for Pd–Cu (1:1)/RGO (a) and Pd–Cu (1:1)/RGO-1 (b) and Pd/RGO (c) modified electrodes in 1 M KOH/1 M CH₃CH₂OH solution.

RGO had the best catalytic activity with peak current densities of 1153.4 and 2105.4 mA mg⁻¹ Pd for methanol and ethanol electro-oxidation, respectively. In addition, the Pd–Cu (1:1)/RGO showed good catalytic stability. This work proves that catalytic activity of Pd catalyst can indeed be improved through control not only on Pd NP size and shape but also on its composition. Therefore the Pd–Cu/RGO hybrids should be very useful for use in direct methanol and ethanol fuel cells.

References