One-Pot Synthesis of Hierarchical Flower-Like Pd-Cu Alloy Support on Graphene Towards Ethanol Oxidation

Jingyi Zhang, Anni Feng, Jie Bai, Zhibing Tan, Wenyao Shao, Yang Yang, Wenjing Hong and Zongyuan Xiao*

Abstract

The synergetic effect of alloy and morphology of nanocatalysts play critical roles towards ethanol electrooxidation. In this work, we developed a novel electrocatalyst fabricated by one-pot synthesis of hierarchical flower-like palladium (Pd)-copper (Cu) alloy nanocatalysts supported on reduced graphene oxide (Pd-Cu/F/RGO) for direct ethanol fuel cells. The structures of the catalysts were characterized by using scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectrometer (XPS). The as-synthesized Pd-Cu/F/RGO nanocatalyst was found to exhibit higher electrocatalytic performances towards ethanol electrooxidation reaction in alkaline medium in contrast with RGO-supported Pd nanocatalyst and commercial Pd black catalyst in alkaline electrolyte, which could be attributed to the formation of alloy and the morphology of nanoparticles. The high performance of nanocatalyst reveals the great potential of the structure design of the supporting materials for the future fabrication of nanocatalysts.

Keywords: Pd nanocatalyst, Flower-like, Ethanol oxidation, Direct ethanol fuel cells

Background

Direct ethanol fuel cells (DEFCs) are considered as economic and environment-friendly renewable energy sources because of the low operating temperature, renewability, low toxicity, and high energy density [1, 2]. Long-term activity has remained as a tremendous challenge for future application of DEFCs, while the poisoning becomes the bottleneck for further improvement. Among all metal nanocatalysts, Pd attracts more attention not only because of its lower cost but also its little CO poisoning effects for electrochemical oxidation of ethanol [3, 4]. In addition, it is reported that morphology and structures of supporting materials or nanoparticles might significantly influence their electrochemistry properties [5, 6], and the following have been studied: micro/nanoleaves [7], nanoflowers [6], nanowires [8], hierarchical hollow microsphere [9], and flower/grass-like structures [10]. The hierarchical flower-like copper is recently reported by changing the morphology of copper to acquire a large surface area [5, 11, 12]. It is also found that copper not only reduce the cost of electrocatalyst but also can be more preferable for the adsorption of hydroxyls, which further increases the rate of alcohol oxidation [4, 13]. Moreover, the electronic properties would be changed due to the d-band center shifts during the formation of Pd-Cu alloy, and the synergetic effect of the composition further increase the electrocatalytic activity towards ethanol [14, 15].

Besides metallic materials, the ideal supporting materials of electrocatalysts are expected to have high surface area and good electrical conductivity [16, 17], and recently, series of graphene and its complex materials are developed as supported materials for the nanocatalysts towards ethanol oxidation. It was reported that metals could be well dispersed on the graphene due to the large numbers of functional groups on the graphene layers that exhibited high catalytic activity for electrooxidation of alcohol [15, 16, 18]. Therefore, it would be promising to
develop a flower-like Pd-Cu alloy nanocatalysts supported on reduced graphene oxide towards electrochemical oxidation of ethanol.

Herein, we developed a facile one-pot hydrothermal approach to prepare flower-like Pd-Cu alloy nanoparticles supported on reduced graphene oxide (RGO). The addition of ammonia solution not only influence the formation of Pd-Cu alloy but also lead to the hierarchical flower-like structure, attaching to the RGO surface, synergistically increasing the surface area of electrocatalysts and acquiring more available active sites [19]. The Pd-Cu(F)/RGO nanocatalyst was characterized by scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray photoelectron spectrometer (XPS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and thermogravimetric analysis (TGA). The electrochemical studies in alkaline medium show that the Pd-Cu(F)/RGO nanocatalyst provides higher activity and significantly better long-term activity towards ethanol electrooxidation than RGO-supported Pd nanocatalyst and commercial Pd black.

Methods
Reagent and Chemicals
Copper(II) nitrate trihydrate (Cu(NO_3)_2·3H_2O), palladium chloride (PdCl_2), ethylene glycol (EG), ethanol, graphite powder (S.P.), sulfuric acid (98 wt% H_2SO_4), potassium permanganate (KMnO_4), and potassium borohydride (95 wt% KBH_4) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrogen peroxide (30 wt% H_2O_2) and ammonia solution were provided by Guangdong Guanghua Sci Tech Co., Ltd. Sodium hydroxide (NaOH) was offered by Aladdin Industrial Inc. Polyvinylpyrrolidone (PVP, MW = 30,000, A.R.) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ten percent of Pd black was provided by HESEN Electric Co., Ltd. (Shanghai, China). Five weight percent of Nafion solution was obtained from Sigma Aldrich. All chemicals were used without any further purification.

Preparation of the Pd-Cu(F)/RGO
Preparation of Graphene Oxide (GO)
GO was prepared from graphite powder according to a modified Hummers method [20].

Preparation of Pd-Cu(F)/RGO
Firstly, a mixed solution of 40 mL EG and 40 mL ethanol was prepared, and 160 mg of PVP was put into the solution under sonication for 30 min, then adding 0.01 mol L^{-1} PdCl_2 and 0.02 mol L^{-1} Cu(NO_3)_2·3H_2O into the mixed solution under stirring, following by adding a certain volume of ammonia solution to adjust pH = 10.0. Next, 30 mg of as-prepared GO was dispersed in the mixed solution of 5 mL EG and 5 mL ethanol under sonication condition to form GO suspension, then adding them to the solution mentioned above with sonication for another 60 min. After these steps, we transferred the mixture solution with 2 mL KBH_4 (0.15 mg mL^{-1}) into a 50-mL Teflon-lined autoclave and maintained at 160 °C for 6 h. After cooling down to the room temperature, the product was centrifuged and washed for several times with ultrapure water and ethanol. At last, the product was dried at 40 °C in a vacuum overnight; the result was named Pd-Cu(F)/RGO.

We also prepared the spherical particle Pd and Cu supported on RGO nanocatalyst in the similar method mentioned above, while the difference is that ammonia solution was replaced by Na_2CO_3 solution. The catalysts obtained were marked as Pd-Cu(F)/RGO. And the RGO-supported Pd (Pd/RGO) or Cu (Cu(F)/RGO) nanocatalysts were also prepared under similar conditions without Cu(NO_3)_2·3H_2O or PdCl_2, respectively.

Electrochemical Measurements
The electrochemical measurements for electrocatalytic activity and stability of catalysts were performed on an electrochemical work station CHI750D by using a three-electrode cell at room temperature. A platinum plate electrode was used as the counter electrode, while a saturated calomel electrode (SCE) was used as the reference electrode. The preparation of working electrode was the following steps: 2 mg of Pd-Cu(F)/RGO catalyst was added into 2 mL ultrapure water under sonication to form a suspension; then, 10 µL of the catalyst suspension was spread on the surface of a glassy carbon electrode (GCE, 5 mm in diameter), which has been carefully polished with alumina powders and cleaned with ultrapure water. Later, 5 µL Nafion solution (5 wt%) was dropped on the surface as a layer to cover the samples. For comparison, the Pd-Cu(F)/RGO, Pd/RGO, and commercial Pd black catalysts were also modified for the electrodes under the same conditions. In each experiment, high-purity nitrogen was used to saturate the electrolyte for 30 min to remove the oxygen.

Results and Discussion
SEM and TEM were employed to investigate the size and morphology of Pd-Cu(F)/RGO, Pd-Cu(F)/RGO, Cu(F)/RGO, and Pd/RGO catalysts. As shown in Fig. 1a, the Pd-Cu alloy nanoparticles are on both sides of the graphene layer. It can be obviously seen from Fig. 1b, c...
that these Pd-Cu (F)/RGO nanocatalysts have a flower-like morphology which is different from particle Pd-Cu(P)/RGO nanoparticles shown in Fig. 1e, f. And the average particle sizes of these two catalysts were approximately 80 ± 5 nm and 10 ± 2 nm, respectively. The morphology of Pd-Cu (P)/RGO is much closer to Cu(F)/RGO nanoparticles shown in Fig. 1g rather than the spherical particle structure of Pd/RGO nanoparticles shown in Fig. 1h, and this compact hierarchical flower-like morphology is just as reported in previous studies, suggesting this structure is relevant to the impact of Cu and ammonia solution [21, 22]. The flower-like Pd-Cu nanoparticles without graphene were also fabricated shown in Fig. 1d to affirm the role of graphene in the electrocatalysts. It can be observed that the nanoparticles dispersed unevenly and some small nanoparticles aggregated together. Compare with the morphology of Pd-Cu(F)/RGO, it can be concluded that graphene is an ideal substrate for supporting and dispersing nanoparticles, which is consistent with previous reports [17, 21].

To investigate the element distribution of the Pd-Cu(F)/RGO, the energy dispersive X-ray spectroscopy (EDX) spectra was shown in Fig. 2a. The results indicated that the weight fractions of Pd and Cu of Pd-Cu(F)/RGO was approximately 1:1.4, which agreed with the feeding weight fractions of Pd and Cu which were 1:1.3. The actual weight fractions were further measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), and the analysis result revealed that Pd-Cu(F)/RGO contains 15.8 wt% Pd and 21.4 wt% Cu, which was roughly consistent with EDX. The STEM-EDS scanning profiles (Fig. 2b) also indicated that Pd and Cu elements were loading on the catalysts homogeneously.

The XRD patterns of the Pd-Cu(F)/RGO, Pd-Cu(P)/RGO, Pd/RGO, and Cu(F)/RGO catalysts were presented in Fig. 3. For the Pd-Cu(P)/RGO, three diffraction peaks were detected at 40.1°, 46.9°, and 68.6°, corresponding to the (111), (200), and (220) crystallite planes of Pd, which were consistent with the peaks of Pd/RGO. And the diffraction
peak at 43.3° belongs to the (111) planes of the Cu, suggesting the phase separation between monometallic Pd and Cu in Pd-Cu_{1p}/RGO. The peak positions of the Pd-Cu_{1p}/RGO shifted in comparison with Pd/RGO, suggesting the formation of Pd-Cu alloys [12]. The control experiment of Cu_{1p}/RGO without Pd loading shows additional peaks at 29.6°, 42.4°, 61.4°, and 74.0° corresponding to Cu_{2+1 O(Cu_{2}O with metal excess defects), which confirmed that the copper was loaded on the RGO and oxidized. Moreover, the broad peak at around 25° is detected in each line, which is attributed to the (002) planes of RGO, suggesting the removal of oxygen-containing functional groups from the GO [23].

To further determine the structure, XPS analysis was performed to analyze the surface chemical states and the components of the sample. The high-resolution XPS spectra of Pd 3d, Cu 2p regions of Pd-Cu_{1p}/RGO are shown in Fig. 4a, b, respectively. The XPS spectrum of Pd was a combination of four peaks that came from Pd at 340.6 and 335.2 eV and PdO at 341.6 and 336.2 eV [4]. In Cu XPS spectrum, the peaks at around 932.6 and 952.6 eV represented Cu 2p3/2 and Cu 2p1/2, respectively. The Cu 2p3/2 and Cu 2p1/2 signals were fitted with six peaks that can be due to Cu or Cu_{2}O at 932.4 and 952.4 eV, CuO at 933.2 and 953.2 eV, and Cu(OH)_{2} at 934.4 and 955.2 eV, which were partly consistent with the result of XRD.

According to the XPS data, we proposed the possible formation mechanism as follows: In the solution of ammonia, both Cu^{2+} and Pd^{2+} were coordinated with the ammonia, forming the [Cu(NH_{3})_{4}]^{2+} and [Pd(NH_{3})_{4}]^{2+}, respectively. A fraction of the complexes further combined with OH\(^{-}\) to form the metal oxides [24], and the other part, was reduced by KBH_{4} to nanoparticles. During this process, Pd-Cu alloy was formed. It is possible that the adding of ammonia favors the formation of Pd-Cu alloy [25, 26]. We believe the PVP plays a crucial role as a structure-directing agent during the reduction, which is similar to the system of the Pt-Cu under the circumstance of cetyltrimethylammonium bromide (CTAB). CTAB and PVP are usually used to control the nucleation and growth of nanoparticles and influence the reaction rate, resulting in various shapes [27–29]. Meanwhile, GO was reduced to RGO by KBH_{4} and the flower-like Pd-Cu alloy nanoparticles were deposited on the RGO due to the strong interactions between metal or metal oxide nanoparticles and the functional groups of RGO [1]. The schematic of the preparation of Pd-Cu_{1p}/RGO nanostructures was shown in Fig. 5. As for Pd-Cu_{1p}/RGO, according to the works of Zhang QL et al. [1] and Lu L et al. [30], Pd^{2+} and Cu^{2+} can be reduced by KBH_{4} and deposited on the RGO, as well as Na_{2}CO_{3} by just adjusting the pH of the system.

Thermogravimetric analysis (TGA) was performed under a flow of air, and the samples were heated with
a heating rate of 10 °C min\(^{-1}\). The analysis was conducted on Pd-Cu(F)/RGO, Pd-Cu(P)/RGO, Pd/RGO, and GO. The results shown in Fig. 6 illustrated that a weight loss of about 6% of Pd-Cu(F)/RGO occurred between 250 and 500 °C, while the weight loss of Pd-Cu(P)/RGO was about 14% and Pd/RGO was around 22%. The weight loss of products in air atmosphere at high temperature was probably due to the removal of the remaining oxygen-containing functional groups. The significant weight loss of GO, around 28% between 100 and 300 °C, was mainly due to the removal of oxygen-containing functional groups, just like C–O and C=O. And the weight loss within 100 °C which came from the escape of water molecules between the RGO nanosheets as well as the weight loss above 500 °C was due to the combustion of carbon skeleton [27, 31, 32]. The result indicated the removal of the oxygen-containing functional groups on Pd-Cu(P)/RGO and Pd-Cu(F)/RGO, which further confirms that GO was efficiently reduced to RGO during the synthesis [23].

To evaluate the performance of these catalysts for ethanol electrooxidation in alkaline medium, the electrochemical behavior of these catalysts was investigated by cyclic voltamograms (CV) in 0.5 M NaOH solution without and with 0.5 M C\(_2\)H\(_5\)OH. The CVs measured in a N\(_2\)-saturated 0.5 M NaOH solution at a scan rate of 50 mV s\(^{-1}\) were shown in the Fig. 7a. The CV measurements were carried out between −0.8 and 0.2 V (vs. SCE), and the peaks from −0.2 to 0 V were contributed by the formation of oxygenated species on the surface of Pd, and the peaks between −0.4 and −0.2 V were mainly due to the reduction of PdO, which can release surface sites for ethanol oxidation [2]. The electrochemical active surface area (ECSA) was calculated by the integral area of the reduction of PdO. The ECSA was estimated to be 151.90 m\(^2\) g\(^{-1}\) Pd for the Pd-Cu(F)/RGO, which was larger than that for the Pd-Cu(P)/RGO (123.36 m\(^2\) g\(^{-1}\) Pd), Pd/RGO (102.66 m\(^2\) g\(^{-1}\) Pd), and Pd black (88.10 m\(^2\) g\(^{-1}\) Pd).

The CVs of Pd-Cu(F)/RGO, Pd-Cu(P)/RGO, Pd/RGO, and Pd black in a N\(_2\)-saturated 0.5 M NaOH + 0.5 M C\(_2\)H\(_5\)OH solution were shown in Fig. 7b. The ethanol oxidation current of Pd-Cu(F)/RGO (2416.25 mA mg\(^{-1}\) Pd) was higher than that of Pd-Cu(P)/RGO (1779.09 mA mg\(^{-1}\) Pd).
Pd), and much higher than Pd/RGO (997.70 mA mg⁻¹ Pd) and Pd black (847.4 mA mg⁻¹ Pd), which means the Pd-Cu(F)/RGO had high activity of ethanol oxidation. There were also different onset potentials of ethanol oxidation among the four catalysts. The onset potential of Pd-Cu(F)/RGO was more negative than that of Pd-Cu(P)/RGO while much more negative than that of Pd/RGO and Pd black. This observation implied that ethanol molecules can be more easily oxidized on Pd-Cu(F)/RGO. We can conclude that the as-prepared flower-like catalysts had better electrochemical performance than the synthetic spherical particle catalysts.

To reveal the role of Cu in the Pd-Cu(F)/RGO, a control experiment of Cu(F)/RGO without Pd loading was performed under the same condition. As shown in the inset of Fig. 7a, b, there was no obvious peak of ethanol oxidation in the CV curve of Cu(F)/RGO in 0.5 M NaOH + 0.5 M C₂H₅OH. This result was consistent with the previous reports [4, 12]. The ignorable electrocatalytic activities towards ethanol oxidation of Cu(F)/RGO suggested that the Pd acted as the active sites for the electrocatalytic oxidation towards ethanol electrooxidation, and the formation of Pd-Cu alloy can further improve the electrocatalytical activity [33]. The role of Cu in the Pd-Cu(F)/RGO in the electrooxidation reaction can be explained by bi-functional effect [12]. Cu is an electron donor atom, while Pd is an electron acceptor. The d-band center shifts when alloying is done between Pd and Cu, and this phenomenon may increase the electrocatalytic oxidation [18, 34, 35]. Therefore, the formation of Pd-Cu alloy will be in favor of ethanol electrooxidation. It is also interesting that the change of morphology from particle to hierarchical flower-like structure also further improves the electroactivity, which is mainly due to the large surface area and increase in the number of catalytic active sites [36].

The durability test of these four catalysts were measured in a N₂-saturated 0.5 M NaOH + 0.5 M C₂H₅OH solution for 3000 s at a potential of −0.35 V, as shown in Fig. 8. Because of the formation of the intermediate species, the initial currents dropped quickly at the beginning [1], and the rate of decay for Pd-Cu(F)/RGO was significantly smaller than that of Pd-Cu(P)/RGO. The final current after 3000 s of Pd-Cu(F)/RGO was much higher than that of Pd-Cu(P)/RGO, Pd/RGO, and Pd black under the same conditions, and the values of current density were list in Table 1. These results illustrated the highest long-term electrocatalytic activity of Pd-Cu(F)/RGO among the investigated catalysts, which suggested that the formation of hierarchical flower-like morphology and alloying significantly improve the stability of catalysts towards ethanol electrooxidation.

Conclusions

In summary, we developed a one-pot synthesis approach for the preparation of a novel hierarchical flower-like Pd-Cu alloy nanocatalysts supported on
Table 1  Peak current densities of various catalysts in 0.5 M NaOH + 0.5 M C₂H₅OH at a sweep rate of 50 mV s⁻¹, 25 °C

| Catalyst         | j/mA mg⁻¹ Pd | Final current/initial current |
|------------------|--------------|------------------------------|
| Pd-Cu₄P/RGO      | 441.25       | 10 s                         |
|                  | 250.75       | 1000 s                       |
|                  | 195.63       | 2000 s                       |
|                  | 146.94       | 3000 s                       |
| Pd-Cu₄P/RGO      | 387.52       |                              |
| Pd/RGO           | 393.54       |                              |
| Pd black         | 213.93       |                              |

chemical converted graphene. It is found that the addition of ammonia solution during the preparation of nanocatalysts offers the opportunity to tune the morphology of nanocatalysts and influence the formation of alloy, both of which lead to highly enhanced electrocatalytic activity towards the ethanol oxidation in alkaline medium and better long-term stability of the hierarchical flower-like structure of Pd-Cu₄P/RGO than that of the Pd-Cu₄P/RGO, Pd/RGO, and Pd black catalysts. The significantly enhanced electrocatalytic activity and durability benefiting from the hierarchical flower-like morphology and Pd-Cu alloy suggest that the Pd-Cu₄P/RGO could be promising an electrocatalyst towards ethanol oxidation in DEFCs, revealing the great potential of the structure design of the supporting materials for the future fabrication of nanocatalysts.

Abbreviations
Cux Copper; CVs: Cyclic voltammograms; DEFCs: Direct ethanol fuel cells; ECSA: Electrochemical active surface area; GCE: Glassy carbon electrode; GO: Graphene oxide; ICP-OES: Inductively coupled plasma optical emission spectroscopy; Pd: Palladium; RGO: Reduced graphene oxide; SCE: Saturated calomel electrode; SEM: Scanning electron microscopy; TEM: Transmission electron microscope; TGA: Thermogravimetric analysis; XPS: X-ray photoelectron spectrometer; XRD: X-ray diffraction

Acknowledgements
This work was generously supported by ‘NSFC’ (project numbers 51576168 and 21503179) and Young Thousand Talent Project of China.

Authors’ Contributions
ZX supervised the project and participated in the design of the study. JZ did the synthetic and characteristic job in this manuscript and edited the manuscript. AF, JB, and ZT helped with the analysis of the mechanism. WS, YY, and WH gave the advice and guide for the experimental section. WH also revised the manuscript. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

Publisher’s Note
Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
19. Hasan M, Newcomb SB, Rohan JF, Razeeb KM (2012) Ni nanowire supported 3D flower-like Pd nanostructures as an efficient electrocatalyst for electrooxidation of ethanol in alkaline media. J Power Sources 218:148–156
20. Jr WSH, Offeman RE (1958) Preparation of graphitic oxide. J Am Chem Soc 80(6):1339
21. Liu S, Tian J, Wang J, Luo Y, Sun X (2012) One-pot synthesis of CuO nanoflower-decorated reduced graphene oxide and its application to photocatalytic degradation of dyes. Catal Sci Technol 2(2):339–344
22. Li H, Yu S, Han X (2016) Fabrication of CuO hierarchical flower-like structures with biomimetic superamphiphobic, self-cleaning and corrosion resistance properties. Chem Eng J 283:1443–1454
23. Lv J, Liu S, Wang A, Mei LP, Feng JJ, Chen JR, Chen Z (2014) One-pot synthesis of monodisperse palladium-copper nanocrystals supported on reduced graphene oxide nanosheets with improved catalytic activity and methanol tolerance for oxygen reduction reaction. J Power Sources 269:104–110
24. Qin Y, Che R, Liang C, Zhang J, Wen Z (2011) Synthesis of Au and Au–CuO cubic microcages via an in situ sacrificial template approach. J Mater Chem 21(11):3960
25. Liu H, Zhang Z, Qian Y, Zhang M (1999) Preparation and characterization of ultrafine powders of Cu-Pd alloy by y-radiation. Chinese Journal of Chemical Physics
26. Liu J, Wu Q, Huang F, Zhang H, Xu S, Huang W, Li Z (2013) Facile preparation of a variety of bimetallic dendrites with high catalytic activity by two simultaneous replacement reactions. RSC Adv 3(34):14312
27. Xia BY, Wu HB, Wang X, Lou XW (2012) One-pot synthesis of cubic PdCu3 nanocages with enhanced electrocatalytic activity for the methanol oxidation reaction. J Am Chem Soc 134(34):13934–13937
28. Yu X, Wang D, Feng Q, Li Y (2011) High performance electrocatalyst: Pt-Cu hollow nanocrystals. Chem Commun (Camb) 47(28):8094–8096
29. Amornkitbamrung L, Piyapinijtham P, Thammacharoen C, Ekgast S (2015) Formation and self-assembly growth of palladium nanospheres into flowerlike microstructures using hydrogen peroxide as a sole reducing and shape-controlling agent. J Nanopart Res 17(11):1–11
30. Lu L, Shen L, Shi Y, Chen T, Jiang G, Ge C, Tang Y, Chen Y, Lu T (2012) New insights into enhanced electrocatalytic performance of carbon supported Pd-Cu catalyst for formic acid oxidation. Electrochim Acta 85:187–194
31. Yuan M, Liu A, Zhao M, Dong W, Zhao T, Wang J, Tang W (2014) Bimetallic PdCu nanoparticle decorated three-dimensional graphene hydrogel for non-enzymatic amperometric glucose sensor. Sensors Actuators B Chem 190:707–714
32. Li J, Tang W, Huang J, An J, Mo J (2013) Polyethyleneimine decorated graphene oxide-supported Ni1−xFe x bimetallic nanoparticles as efficient and robust electrocatalysts for hydrazine fuel cells. Catal Sci Technol 3(12):3155
33. Shang L, Zhao F, Zeng B (2014) 3D porous graphene–porous PdCu alloy nanoparticles–molecularly imprinted poly (para-aminobenzoic acid) composite for the electrocatalytic assay of melamine. ACS Appl Mat Interfaces 6(21):18721–18727
34. Mandal K, Bhattacharjee O, Roy PS, Bhattacharya SK, Dasgupta S (2015) Room temperature synthesis of Pd–Cu nanoalloy catalyst with enhanced electrocatalytic activity for the methanol oxidation reaction. Appl Catal A-Gen 492:100–106
35. Pozun ZD, Rodenbusch SE, Keller E, Tran K, Tang W, Stevenson KJ, Henkelman G (2013) A systematic investigation of p-nitrophenol reduction by bimetallic dendrimer encapsulated nanoparticles. J Phys Chem C Nanomater Interfaces 117:7598–7604
36. Huang L, Han Y, Dong S (2016) Highly-branched mesoporous Au-Pd-Pt trimetallic nanoflowers blooming on reduced graphene oxide as an oxygen reduction electrocatalyst. Chem Commun (Camb) 52(56):8659–8662