International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

# **Pt-Pd Bimetallic Nanocomposites Catalyst Formed on Graphene Surface: Preparation and high-performance for Methanol Electro-Oxidation**

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Received: 5 April 2021/ Accepted: 23 May 2021 / Published: 30 June 2021

Reduced graphene oxide (RGO) supported Pt-Pd bimetallic nanocomposites with "clean surface" were prepared by direct electrodeposition method on glassy carbon electrode (GCE). The obtained Pt-Pd decorated RGO nanohybrids were characterized by field emission scanning electronic microscope (FE-SEM), X-ray photoelectron spectroscopy (XPS), and electrochemical method. The results have showed that the synergistic effect of alloying with Pd in the Pt-Pd nanoclusters structure leads to much higher performance for methanol oxidation reaction (MOR) than pristine Pt nanoparticles. Moreover, with the support of RGO, the Pt-Pd nanocomposites show much better durability and high efficiency in MOR. This work can help us deeply understand the electrocatalytic mechanism for MOR and will benefit the selection of new catalysts with high efficiency and low cost.

Keywords: Pt-Pd nanoclusters, graphene, methanol electrooxidation

# **1. INTRODUCTION**

The rapid growth of energy consumption and the solid issues related to the use of fossil fuels inspired people to seek for alternative energy sources. Among them, fuel cell is one of the promising types due to its easier storage.[1-4] It is well-known that platinum (Pt) is the most commonly used catalyst used for methanol oxidation reaction (MOR), but the high cost and easy poisoning have limited the wide applications.[4-7] Therefore, conductive substrate-supported bimetallic nanostructures are prepared to substitute Pt catalyst for enhancing conversion efficiency and catalytic tolerance in MOR.[6-9] For example, activated carbon,[10,11] carbon nanotubes,[12-14] conductive polymers,[2,15] and grapheme[16,17] have been selected as substrates to load bimetallic nanoparticles for electro-catalyzing MOR with high performance.

Graphene, the one-atom thick planar sheet of hexagonally arrayed  $sp^2$  carbon material, has excellent conductivity and mechanical strength in catalysts, sensors, photovoltaics and so on.[6,18-24] Graphene sheets have theoretical surface areas about 2600 m<sup>2</sup>/g[19], making this material an excellent choice for use as electrochemical sensors or biosensors support.[6,23,24] Meanwhile, depositing of two or more nanoparticles onto the same reduced graphene oxide(RGO) sheet as independent sites can provide greater performance in carrying out electro-catalyst or sensing processes.[6,22-24]

Inspired by the need for low-cost catalysts and sensitive sensors, the study of inexpensive bimetallic nanoparticles has become more and more important.[7,8,13,25] Herein, a facile method was developed for synthesizing Pt-Pd bimetallic nanocomposites (NCs) with relatively "clean surface" uniformly dispersed on RGO surface by in-situ electrodeposition technique. The result revealed that the Pt-Pd bimetallic NCs had good electrocatalytic activity towards methanol oxidation reaction (MOR) with high stability and reproducibility. This kind of high electrocatalytic activity may be due to the synergistic effect of Pt-PdNCs and the special functional groups on the RGO surface.[26-28]

# 2. EXPERIMENTAL

#### 2.1. Materials and reagents

Hexachloroplatinic (IV) acid ( $H_2PtCl_6 \cdot 6H_2O$ , 99.9%), methanol (99.9%), Palladium (II) chloride (PdCl<sub>2</sub>, AR) were obtained from Sangon Biotech (Shanghai, China). Reduced grapheneoxide(RGO) was provided by Xianfeng Nanomaterials Tech.(Nanjing, China), which was prepared from graphene oxide(GO) firstly,[29,30] and then reduced by hydrazine.[31] All water used in experiments was double-distilled water.

# 2.2. Apparatus

An electrochemical workstation (CHI660D mode, CHI, Shanghai, China) was used to do electrochemical tests, such as Cyclic voltammogram (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry. A glassy carbon electrode (GCE,  $\varphi = 3.00$  mm) serves as a working electrode and aplatinum wire was used as a counter electrode. And all potentials were converted to values with reference to an Ag/AgCl electrode (3 M KCl). A JSM-6700F mode microscope (JEOL, Japan) was used to record Field-emission scanning electron microscopy (FE-SEM) images. All experiments were carried out at 25 °C.

#### 2.3. Fabrication of PtPd/RGO/GCE electrodes

Before being modified, GCE was polished by  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders with the size of 1.0, 0.3, and 0.05  $\mu$ m, successively. After that, the polished GCE was sonicated (water and ethanol for 5 min, respectively) and dried by nitrogen before use.



Scheme 1. Scheme of the fabrication process of Pt-Pd nanocomposites on RGE/GCE surface.

The fabrication steps were provided as Scheme 1. For the fabrication process of Pt-Pd bimetallic nanoclusters on the surface of RGO/GCE, the RGO (1 mg) sheets were dispersed in pure ethanol (1 mL) to form a homogeneous solution firstly. 8  $\mu$ L of RGO solution was dropped on GCE surface by using micro-syringe, and then dried at room temperature. Owing to the  $\pi$ - $\pi$  electronic interactions between GCE and RGO, the RGO was immobilized on GCE surface, and the prepared electrode was denoted as RGO/GCE. After that, the RGO-supported Pt-Pd NCs were electrochemically prepared by CVs in an aqueous solution containing 7.2 mM H<sub>2</sub>PtCl<sub>6</sub>, 0.8 mM PdCl<sub>2</sub> and 1 M HCl in the potential range of -0.24V to 1.2V (vs. Ag/AgCl) for 20 circles (scan rate of 50 mV/s). Finally, the Pt-Pd NCs will be formed on RGO/GCE.[32]

#### **3. RESULTS AND DISCUSSION**

#### 3.1 Formation and characterization of RGO-supported Pt-Pd NCs on GCE

Electrodeposition of Pt-Pd NCs on RGO/GCE was achieved through CV scanning between-0.24V to 1.2V at a scan rate of 50mV/s for 20 cycles, which is shown in Figure S1. From the increase of oxidation/reduction peaks of Pt-Pd (0.9-1.2 V; 0.1-0.5 V) and the absorption/desorption peaks of hydrogen at ~ 0 - -0.2 V, it can be proved that Pt-Pd were electro-deposited on RGO-covered GCE surface successfully. The prepared RGO supported Pt-Pd nanocomposites were characterized by TEM and FE-SEM shown in Figure 1. Figure 1A shows the morphology of RGO sheets with typical crumpled and wrinkled shape because of their thermo-dynamic stability. Figure 1B reveals the formation of Pt-Pd nanoclusters with average diameter of 200 nm and the small nanoparticles on clusters surface can be observed clearly.



Figure 1. (A) TEM image of RGO on the GCE surface. (B) FE-SEM image of Pt-Pd nanocomposites modified on RGO/GCE surface.

XPS data were also provided to investigate the Pt-Pd NCs on RGO modified glass carbon chip (see Figure 2). The high-resolution scans of C 1s, Pd 3d and Pt 4f regions were provided in Figure 2B, 2C and 2D, respectively. The Pt4f<sub>5/2</sub> Pt4f<sub>7/2</sub>, Pd3d<sub>3/2</sub> and Pd3d<sub>5/2</sub> peaks were located at a binding energy of 74.4 eV, 71.0 eV, 340.3 eV and 335.0 eV, corresponding to zero-valent Pt and Pd.[25,27]

CVs were utilized to reveal the electrochemical properties of prepared electrodes. A pair of quasi-reversible redox peaks with a peak separation ( $\Delta E_p$ ) of 106 mV could be observed from bare GCE in K<sub>3</sub>[Fe(CN)<sub>6</sub>] aqueous solution (see Figure 3A). The peak current increased slightly and the  $\Delta E_p$  reduced to 102 mV after the electrode modified with RGO. The peak current continues increasing and the  $\Delta E_p$  reduced to 76 mV, 77 mV, 68 mV, 64 mV, at the Pd/RGO/GCE, Pt/RGO/GCE, Pt-Pd/GCE and Pt-Pd/RGO/GCE respectively. The CVs results demonstrated that the Pt-Pd NCs and RGO were modified on the surface of GCE successfully.



Figure 2. XPS spectra of (A) Pt-Pd NCs, (B) Pd 3d, (C) C 1s, (D) Pt 4f modified on RGO/GCE surface.



Figure 3. (A)Complex plane impedance plots in 5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]:K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1:1) mixture containing 0.1 M KCl at bare GCE (a), RGO/GCE (b), Pd/RGO/GCE(c), Pt/RGO/GCE(d), Pt-Pd/GCEI and Pt-Pd/RGO/GCE(f) respectively. (B) CVs of 5.0 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] + 0.1 M KCl at bare GCE (a), RGO/GCE (b), Pd/RGO/GCE(c), Pt/RGO/GCE(d), Pt-Pd/GCEI and Pt-Pd/RGO/GCE(f), respectively. Scan rate: 50 mVs<sup>-1</sup>.

Our previous research has demonstrated that EIS is a useful tool for characterizing electrode surface modification by use of the redox probe of Fe(CN)<sub>6</sub><sup>3-/4</sup>.[25,33] Figure 3B presents the EIS of bare GCE, RGO/GCE, Pt/GCE, Pd/RGO/GCE, Pt/RGO/GCE, Pt-Pd/GCE and Pt-Pd/RGO/GCE respectively. The value of electro-transfer resistance (R<sub>et</sub>) can be estimated as the diameter of the semicircle. Figure 3B showed the order of R<sub>et</sub> values was Pt-Pd/RGO/GCE < Pt-Pd/GCE < Pt/RGO/GCE < Pd/RGO/GCE < RGO/GCE < GCE, indicating that PtPd/RGO/GCE had the best conductivity (~40 $\Omega$ ). The R<sub>et</sub> value for modified electrodes decreased dramatically in comparison with GCE, which should be due to the excellent electron transfer property of RGO and Pt-Pd nanoclusters and also indicated that RGO and Pt-Pd had been deposited to GCE surface successfully, which was in good agreement with the CV data shown in Figure 3A.

Figure S2 shows the CV curves of different modified GCEs obtained from -0.24 to 1.4V (*vs.* Ag/AgCl) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The appearance of oxide at high anodic potentials (>0.7 V) and the cathodic removal of oxide at ~0.5 V demonstrated the formation of Pt-Pd NCs. For the Pt-Pd nanoclusters, they are similar to the shapes of voltammograms of pure Pt group metals.[32,34] For Pt NPs, two oxidation peaks (labeled as 1 and 2) can be distinguished in hydrogen desorption region. In the case of the present of Pd, these peaks are interpreted in different ways.[35] Surface area of Pt electrodes can be determined by characteristic value of the charge density associated with a monolayer of hydrogen adsorbed on polycrystalline platinum (210  $\mu$ C/cm<sup>2</sup>).[36] The results from Figure S2 indicate that the PtPd/RGO/GCE has the largest surface areas (0.34 cm<sup>2</sup>), compared to the PtPd/GCE (0.25 cm<sup>2</sup>), and Pt/RGO/GCE (0.13 cm<sup>2</sup>).

#### 3.2. Electrocatalytic MOR at Pt-Pd/RGO/GCE



**Figure 4.** (A) CV curves of GCE (a), RGO/GCE (b), Pd/RGO/GCE(c), Pt/RGO/GCE(d), PtPd/GCEI and Pt-Pd/RGO/GCE(f) in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH at scan rate of 50 mV/s. (B) Chronoamperometric responses of the Pt/RGO/GCE (blue curve), Pt-Pd/GCE (azure curve) and Pt-Pd/RGO/GCE(violet curve) in a solution of 0.5 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Fuel cell technology is becoming more and more important for a large variety of technical areas, such as aerospace, stationary power supplies and transportations.[37,38] Herein, it is significant to investigate the possible application of Pt-Pd/RGO/GCE towards MOR. Figure 4A provided the

typical CV responses of MOR at Pt-Pd/RGO/GCE, Pt-Pd/GCE, Pt/RGO/GCE, Pd/RGO/GCE, RGO/GCE, and bare GCE, respectively. No current peaks were observed at bare GCE, RGO/GCE, or Pd/RGO/GCE for MOR, indicating that the above electrodes did not have catalytic activity towards methanol oxidation. However, at Pt-Pd/RGO/GCE, Pt-Pd/GCE and Pt/RGO/GCE, a bell-shape oxidation peak at ~ 0.67 V in the forwards scan and another oxidation peak at ~ 0.49 V in the reverse scan could be observed for MOR.

On Pt-Pd/RGO/GCE, the onset potential for MOR was 0.18 V, which was about 10 mV less positive than that on Pt-Pd/GCE, and about 30 mV less positive than that on Pt/RGO/GCE (shown in Table 1). It is inferred from Figure 4A that Pt-Pd/RGO/GCE (curve f) shows the highest oxidation current than Pt-Pd/RGO (curve e) and Pt/RGO/GCE (curve d). The current density for MOR is 4.29 mA·cm<sup>2</sup>, 3.34 mA·cm<sup>2</sup>, and 0.77 mA·cm<sup>2</sup> at Pt-Pd/RGO/GCE (curve f), Pt-Pd/GCE (curve e) and Pt/GCE (curve d), indicating the best performance for MOR at Pt-Pd/RGO/GCE (also can be seen in Table 1). The removal of incompletely oxidized carbonaceous species formed in the forward scan could be estimated through the second oxidation peak,[39,40] and the current ratio (If/Ib) of anodic peaks between the forward sweep and the reverse sweep could be utilized to estimate the catalyst tolerance to the accumulation of intermediate species. Higher ratio value (If/Ib) means more tolerant towards CO poisoning.[40] From Table 1, it can be observed that the Pt-Pd/RGO/GCE has the largest value of If/Ib, which also means the best catalytic efficiency from RGO-supported Pt-Pd NCs.

Samples	Current density (mA cm <sup>-2</sup> )	Onset potential of methanol oxidation vs. Ag/AgCl (V)	I <sub>f</sub> /I <sub>b</sub> ratio
Pt/RGO/GCE	0.77	0.21	1.26
Pt-Pd/GCE	3.34	0.19	1.27
Pt-Pd/RGO/GCE	4.29	0.18	1.35

**Table 1.** The current density, onset potential of methanol and If/Ib ratio towards MOR at Pt/RGO/GCE,<br/>PtPd/GCE and PtPd/RGO/GCE obtained from Figure 4A.

The stability of RGO-supported Pt-Pd NCs catalyst was evaluated and the results were shown in Figure 4B, which showed that the RGO-supported Pt-Pd NCs had much higher initial current density than Pt-Pd and Pt/RGO. All the catalysts exhibited a quick current decay after several minutes due to the formation of intermediate species like CH<sub>3</sub>OH<sub>ads</sub> and CHO<sub>ads</sub>,[41,42] while RGO-supported Pt-Pd NCs had the highest current density, indicating that Pt-Pd/RGO/GCE had the best stability and could be used in fuel cell applications. We also tested the durability of the RGO-supported Pt-Pd NCs through 1000 cycles for MOR (shown in Figure S3). The peak current density of the Pt-Pd/RGO/GCE after 1000 cycles was only slightly lower than the original, which also demonstrated that the Pt-Pd/RGO/GCE had the best electrocatalytic stability for MOR.

Finally, in order to evidence the advantages of the present catalyst, the activity of some other Pt based catalysts were listed in Table 2. As we can see, the RGO-supported Pt-Pd NCs displayed a

higher specific activity compared with the Pt/C, PtCu (Ru), PtNi(Ru) as well as PtPd alloys, suggesting that a good potential application in the electrocatalysis.

Catalyst	Specific activity (mA/cm <sup>2</sup> )	Refs.
Pt/C	0.68	
PtCu	1.78	43
PtCuRu	2.31	
PtNiRu nanodendrite	1.79	
PtNiRu nanosphere	1.64	44
PtNi polyhedron	0.85	
$Pt_{3}Pd_{1\_0.21}$	0.99	
$Pt_{3}Pd_{1_{3.11}}$	1.37	45
$Pt_3Pd_{1_5.20}$	0.42	

**Table 2.** Comparison of the activity with some other Pt based catalysts.

# 4. CONCLUSIONS

In conclusion, the Pt-Pd NCs were fabricated on the RGO surface modified on glass carbon electrode. The electrochemical experiments show that RGO-supported Pt-Pd NCs have largely active surface area and good conductivity. The electrocatalysis for MOR shows that the prepared Pt-Pd nanoclusters on RGO surface can oxidize methanol with high efficiency, good stability and durability, which should be found wide applications in fuel cell-based energy fields and electrochemical sensing.

### **ACKNOWLEDGEMENTS**

This work is financially supported by The University Synergy Innovation Program of Anhui Province (GXXT-2019-019), The Key Research and Development Projects of Anhui Province(201904f06020022) and the College Students Innovation and Entrepreneurship Training Program (S201910879301).

#### SUPPORTING INFORMATION



Figure S1. CVs for electrodeposition process of Pt-Pd nanoclusters on RGO/GCE surface in 1 M HCl solution containing  $7.2 \times 10^{-3}$  M H<sub>2</sub>PtCl<sub>6</sub> and  $8 \times 10^{-5}$  M PdCl<sub>2</sub>. Scan rate: 50 mV/s.



**Figure S2.** CVs of 0.5 M H<sub>2</sub>SO<sub>4</sub> at the bare GCE (a), RGO/GCE (b), Pd/RGO/GCE(c), Pt/RGO/GCE(d), Pt-Pd/GCE(e) and Pt-Pd/RGO/GCE(f). Inset: CVs of 0.5 M H<sub>2</sub>SO<sub>4</sub> at the bare Pt electrode respectively. Scan rate, 50 mV/s.



**Figure S3.** CVs of initial Pt-Pd/RGO/GCE and Pt-Pd/RGO/GCE after 1000 cycles in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH at scan rate of 50 mV/s.

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