



# Comparison study of few-layered graphene supported platinum and platinum alloys for methanol and ethanol electro-oxidation



Yi Shen <sup>a,\*</sup>, Kaijun Xiao <sup>a</sup>, Jingyu Xi <sup>b,\*</sup>, Xinping Qiu <sup>b,c,\*\*</sup>

<sup>a</sup> College of Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, China

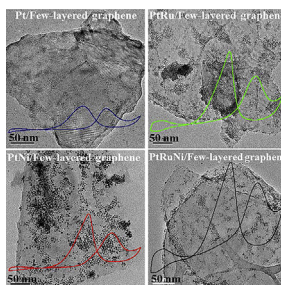
<sup>b</sup> Institute of Green Chemistry and Energy, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

<sup>c</sup> Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China

## HIGHLIGHTS

- Ultrafine Pt, PtRu, PtNi and PtRuNi were assembled to few-layered graphene (FLG).
- The resulting hybrids were studied for methanol and ethanol electro-oxidation.
- The activity followed the sequence of Pt/FLG < PtNi/FLG < PtRu/FLG < PtRuNi/FLG.
- The activity of the catalysts was correlated with the structural characteristics.
- The superior activity of PtRuNi/FLG was attributed to the synergistic effects.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Pt, PtRu, PtNi and PtRuNi nanoparticles are assembled to few-layered graphene (FLG) and the resulting hybrids are examined as catalysts for the electro-oxidation of methanol and ethanol. The structures of the catalysts are characterized using transmission electron microscopy, X-ray diffraction and energy dispersive X-ray spectroscopy. The compositional and electronic properties of the nanoparticles are analyzed using X-ray photoelectron spectroscopy. The activity of the catalysts towards methanol and ethanol electro-oxidation is studied by cyclic voltammetry, linear sweeping voltammetry and chronoamperometry. It is found that the activity of the catalysts follows the sequence of Pt/FLG < PtNi/FLG < PtRu/FLG < PtRuNi/FLG. The activity of the catalysts is well correlated with the structural characteristics. The superior activity of the PtRuNi/FLG catalyst is attributed to the synergistic effects of Pt, Ru and Ni, as explained by the bi-functional, ligand and strain effects.

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## 1. Introduction

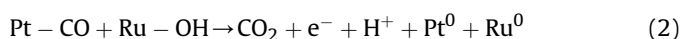
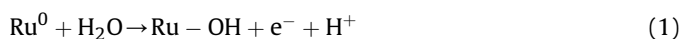
Direct methanol fuel cells (DMFCs) and direct ethanol fuel cells (DEFCs) have stimulated great interest as new power sources for the mobile and portable electronic devices because of the high

\* Corresponding authors.

\*\* Corresponding author. Institute of Green Chemistry and Energy, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China.

E-mail addresses: [feyshen@scut.edu.cn](mailto:feyshen@scut.edu.cn) (Y. Shen), [xijy@tsinghua.edu.cn](mailto:xijy@tsinghua.edu.cn) (J. Xi), [qiuxp@tsinghua.edu.cn](mailto:qiuxp@tsinghua.edu.cn) (X. Qiu).

energy efficiency and low pollution emission [1]. For several decades, tremendous efforts have been directed in developing advanced electrocatalysts to realize the commercialization of DMFCs and DEFCs [2]. So far, Pt has been identified as the most effective element to catalyze the oxidation of methanol and ethanol. However, the utilization of single Pt as catalyst in fuel cells suffers from several problems, such as the sluggish kinetics of the reactions, serious poisoning effects of intermediates and the high cost of the noble metal Pt. To address these issues, Pt-based binary electrocatalysts were extensively studied for the electro-oxidation of methanol and ethanol [3,4]. In particular, PtRu-based electrocatalysts have attracted great attention because of the outstanding catalytic activity [5–7]. The superior activity of PtRu electrocatalysts are always explained by the bi-functional [8,9] and/or ligand effects [10]. The bi-functional mechanism holds that the benefits of Ru addition lie in the generation of Ru–OH species via the activation of water molecules on Ru surface (Equation (1)), which expedites the removal of intermediates adsorbed on Pt surface (Equation (2)).



In contrast, the ligand effect asserts that the main role of Ru is to modify the electronic structure of Pt by interacting with the d-band of Pt. Such modification is presumed to reduce the binding strength of Pt-adsorbate, and subsequently alleviates the poisoning effects of intermediates. In most cases, bifunctional and ligand effects are coexistent in PtRu-based electrocatalysts [10–12]. It is difficult to disentangle these two factors on the enhancement of catalyst performance. In spite of the fact that PtRu is an effective catalyst for the electro-oxidation of methanol and ethanol, nevertheless, both Pt and Ru are quite expensive, leaving room for the development of active but more cost-effective electrocatalysts [8]. Consequently, numerous studies have been conducted to improve the activity of the Pt–Ru system by introducing a third or fourth component. Many ternary PtRuM (M = Mo, Ir, Os, Rh, Sn, Au, Pd, Au, Ni, Co, Fe, etc.) [13–18] and quaternary PtRuMM' (MM' = OsIr, NiZr, MoW, CoW, IrNi, PdOs, etc) [19–24] electro-catalysts were reported for the oxidation of methanol and ethanol. The Pt–Ru–Ni system was widely studied because of its great application potential in fuel cells [25–35]. For instance, Park et al. [25] first systematically studied the activity of Pt, PtRu, PtNi and PtRuNi catalysts for methanol electro-oxidation and revealed the significant effects of Ni in the chemical and electronic structures of the catalysts. Late, the promoting effects of Ni were also confirmed by Wang et al. [26] and Liu et al. [27]. Liang et al. [28] attributed the improved CO-tolerance of the PtRuNi catalyst to the nickel hydroxides, which accelerated the cleavage of CO from Pt surface via the bifunctional mechanism. In addition, Martinez-Huerta et al. [29] found that the activity of PtRuNi/C catalysts was highly dependent on the preparation methods and carbon supports.

To make the best of the active component, supporting materials are utilized to disperse catalyst nanoparticles (NPs). As an ideal catalyst support in fuel cells, it should exhibit a large surface area and excellent conductivity to facilitate the transport of reactants and electrons as well as properly interact with the active component to avoid aggregation. Recently, few-layered graphene (FLG) has been utilized as catalyst supports in fuel cells because of the large surface area, excellent conductivity and corrosion resistance [36]. Numerous Pt/FLG and Pt-based alloy/FLG hybrids were studied as electrocatalysts in fuel cells [37–40]. In the literature, reduced graphene oxide was widely used owing to the presence of oxygen-containing groups such as hydroxyl, epoxides, carbonyl and

carboxyl, which played an important role on anchoring and stabilizing metallic NPs. However, the presence of these oxygen-containing groups also reduced the conductivity and stability of the support. In contrast to reduced graphene oxide, FLG derived from chemical vapor deposition (CVD) contains less oxygen-containing groups and possesses higher conductivity. Up to now, limited studies on using this type of FLG as catalyst support are reported due to the hydrophobic surface [41]. However, it was demonstrated from our previous work that the FLG produced by CVD could be used to stabilize Pt NPs owing to the large number of defects and edges [42]. Herein, Pt, PtRu, PtNi and PtRuNi NPs were assembled to the FLG support and the resulting hybrids were examined as catalysts for the electro-oxidation of methanol and ethanol. The electrochemical characteristics of the electro-oxidation of methanol and ethanol on the catalysts were studied. The objective of this study is to explore the effects of heterogeneous atoms in the catalytic activity of Pt-based electrocatalysts and further correlate the catalytic activity with the structural characteristics.

## 2. Experimental section

### 2.1. Synthesis of catalysts

The FLG support was prepared by CVD and further purified by acid etching and sedimentation separation, as described in our previous work [43]. The catalyst was synthesized using the polyol-assisted reduction method [42]. Briefly, 100 mg of FLG support and 1.2 g of NaOH were added into 150 mL of ethylene glycol under magnetic stirring. After the complete dissolution of NaOH, a predetermined amount of H<sub>2</sub>PtCl<sub>6</sub> aqueous solution, nickel (II) nitrate hexahydrate and ruthenium (III) chloride hydrate were also added into the mixture. The reduction was carried out at 180 °C for 30 min under continuous magnetic stirring. The mixture was separated by centrifuge and thoroughly washed with ethanol. The resulting catalyst was dried at 80 °C overnight. The total metal loading in the catalyst was fixed at ca. 40 wt.% and four samples, i.e., Pt, PtRu, PtNi and PtRuNi supported on the FLG were prepared, which were denoted as Pt/FLG, PtRu/FLG, PtNi/FLG and PtRuNi/FLG, respectively. The nominal atomic ratios of metals were 75:25 (PtRu), 75:25 (PtNi) and 75:15:10 (PtRuNi).

### 2.2. Physical characterization

A transmission electron microscope (TEM) (JEM2010, JEOL) was used to observe the morphology of the samples. An energy dispersive X-ray (EDX) analyzer integrated into the TEM and an axis-ultra X-ray photoelectron spectrometer (Kratos-Axis Ultra System) with monochromatized Al-K $\alpha$  radiation were used to analyze the elemental composition of the samples. To analyze the crystalline structures of the catalysts, X-ray diffraction (XRD) patterns were obtained by a diffractometer (PW1830, Philips) equipped with Cu-K $\alpha$  radiation of 1.54 Å. The *d*-spacing value was calculated from Bragg's law and the average crystal size was determined based on Scherrer formula [44]. The composition of the catalysts was also analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES).

### 2.3. Electrochemical measurements

Electrochemical measurements were carried out using a home-made set-up connected to PARSTAT 2273 electrochemical station (AMETEK, Inc. USA.) The details of the experimental procedures were reported in our previous work [42,45]. A gold patch (effective area 1 cm × 1 cm) coated with a thin layer of catalyst ink was used

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