



# Efficient electrooxidation of biomass-derived glycerol over a graphene-supported PtRu electrocatalyst

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## ABSTRACT

We report very small and highly dispersed PtRu nanoparticles on a graphene support prepared via simple surfactant-free synthesis processes, which demonstrate excellent activity and stability compared with conventional Pt/C and bimetallic PtRu/C for the electrooxidation of biomass-derived glycerol.

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## 1. Introduction

Direct alcohol fuel cells (DAFCs) have attracted a great deal of attention due to their high efficiency and energy density [1]. Recently, oxygenated hydrocarbons such as ethylene glycol and glycerol have also been studied as potential fuels for DAFCs [2]. In particular, glycerol (*Gly*), which can be produced from biomass, is promising due to its low toxicity and inflammability. *Gly* also possesses relatively high theoretical energy density compared to methanol. Most importantly, *Gly* can be produced in a renewable, environmentally friendly, and cost-effective manner [3].

A catalyst with high levels of metal content (i.e., 40 wt.% or more) that is supported on carbon would be a better option as a high performance anode catalyst of DAFCs [4,5]. With catalysts loaded with lower levels of metal, greater amounts of catalysts are required on the electrodes due to sluggish alcohol oxidation kinetics, leading to a thickening of the catalyst layer. The thick catalyst layer would in turn cause greater electric resistance and create a longer transport path between the reactant and the reaction sites. Both of these issues are expected to lead to lower performance. Vulcan XC-72R carbon black has generally been employed as the support material for fuel cells. However, this support has relatively low surface areas of less than 300 m<sup>2</sup>/g [5]. This low surface area may not be sufficient to synthesize the catalyst with high metal loadings. As a potential support material, graphene nanosheets (GNSs) have been synthesized from graphite to

obtain a high specific surface area (theoretically, ca. 2630 m<sup>2</sup>/g) on which small and high metal loaded nanoparticles can be supported [5,6]. Recently, catalytic studies using this GNS support have been reported for methanol electrooxidation and oxygen reduction, demonstrating the possibility for application in fuel cells [5–8].

In this study, we report the use of very small and highly dispersed 60 wt.% PtRu nanoparticles on a GNS support prepared via simple surfactant-free synthesis processes. The PtRu/GNS demonstrates remarkably high performance compared to conventional Pt/C (E-TEK) and bimetallic PtRu/C for *Gly* electrooxidation. This work represents a new attempt at using the 2 dimensional (2D) GNS supports for the development of highly active *Gly* oxidation catalysts.

## 2. Experimental

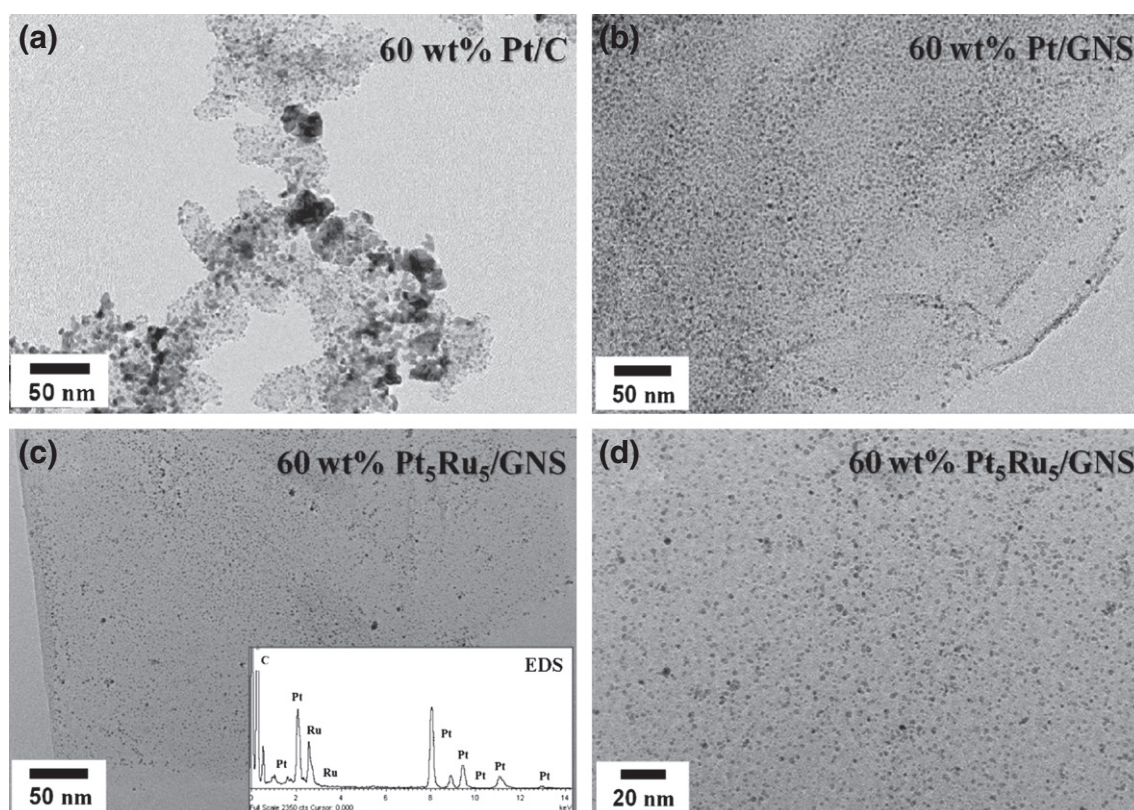
Carbon-supported Pt and PtRu catalysts with 20 and 60 wt.% metal loadings were synthesized as the reference catalysts using the colloidal method combined with freeze-drying process. These catalysts were prepared and used to compare the electrocatalytic performances with the graphene-supported Pt and PtRu catalysts. Details of the synthesis are similar to those that can be found in our previous work [9].

The GNS support was synthesized from graphite as follows: graphite oxide (GO) was synthesized by the chemical oxidation of natural graphite (Carbonix Co., Korea) using H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, P<sub>2</sub>O<sub>5</sub>, and KMnO<sub>4</sub> (Aldrich). The prepared GO was then reduced by thermal exfoliation at 830 °C in a quartz tube under an argon atmosphere for 60 s to form functionalized GNSs. The 60 wt.% PtRu/GNS catalyst was prepared by mixing hydrogen hexachloroplatinate(IV) hexahydrate

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**Fig. 1.** Representative TEM images of the (a) 60 wt.% Pt/C, (b) 60 wt.% Pt/GNS, (c) 60 wt.% PtRu/GNS (the inset in (c) is an EDS spectra of the catalyst) and (d) 60 wt.% PtRu/GNS with higher magnification.

( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ , Aldrich) and ruthenium(III) chloride hydrate ( $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ) in acetone (5 ml) with GNSs (4 mg) and ultrasonicing the mixture for 1 h. The resulting slurry was dried in a convection oven at  $100^\circ\text{C}$  for 5 h to allow the acetone to evaporate. The mixture was then treated with  $\text{N}_2$  gas balanced with 4%  $\text{H}_2$  gas at  $300^\circ\text{C}$  for 2 h.

Electrocatalytic activities for the oxidation of *Gly* were measured over a three-electrode cell at room temperature using cyclic voltammetry (Solartron analytical 1400, AMETEK). A Pt wire and Ag/AgCl (in 3 M KCl) were used as the counter and reference electrodes, respectively. Glassy carbon (with a geometric area of ca.  $0.07\text{ cm}^2$  and a metal loading of  $11.5\ \mu\text{g}$ ) was used as the working

electrode. Cyclic voltammograms (CVs) were subsequently recorded within the potential range of  $-0.2$  to  $1.0\text{ V}$  (vs. Ag/AgCl) at a scan rate of  $50\text{ mV s}^{-1}$ . Chronoamperometry tests of each sample were performed for up to 1000 s at a constant voltage of  $0.6\text{ V}$  (vs. Ag/AgCl).

The structural, chemical and electronic features of the Pt/GNS and PtRu/GNS catalysts were examined using X-ray diffraction (XRD, Rigaku Rotaflex RU-200B) as equipped with a Cu  $\text{K}\alpha$  source ( $\lambda = 1.5405\ \text{\AA}$ ), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100) at 200 K, energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250, UK) using a monochromic Al  $\text{K}\alpha$  X-ray source ( $E = 1486.6\text{ eV}$ ).

**Table 1**

Structural and electronic parameters of the Pt/C, PtRu/C, Pt/GNS and PtRu/GNS catalysts characterized by XRD, TEM and XPS analyses.

Catalysts	$2\theta_{\text{max}}^{\text{a}}$ ( $^\circ$ )	Lattice parameter <sup>b</sup> (Pt–Pt bond distance) ( $\text{\AA}$ )	XRD	TEM	Binding energy (XPS)	
			Crystallite size <sup>c</sup> (nm)	Particle size <sup>d</sup> (nm)	Pt $4f_{7/2}$ (eV)	Ru $3p_{3/2}$ (eV)
20 wt.% Pt/C (E-TEK)	67.68	3.912 (2.766)	2.8	$2.7 \pm 0.6$	71.1 (60) <sup>e</sup> 71.9 (40) <sup>f</sup>	–
20 wt.% Pt <sub>5</sub> Ru <sub>5</sub> /C	68.15	3.889 (2.750)	2.1	$2.1 \pm 0.5$	71.5 (70) <sup>e</sup> 72.4 (30) <sup>f</sup>	462.2 (73) <sup>g</sup> 465.8 (27) <sup>h</sup>
60 wt.% Pt/GNS	67.74	3.909 (2.764)	2.7	$2.2 \pm 0.5$	71.3 (59) <sup>e</sup> 72.5 (41) <sup>f</sup>	–
60 wt.% Pt <sub>5</sub> Ru <sub>5</sub> /GNS	68.10	3.891 (2.751)	2.3	$1.8 \pm 0.3$	71.7 (64) <sup>e</sup> 73.0 (36) <sup>f</sup>	462.0 (58) <sup>g</sup> 464.1 (42) <sup>h</sup>

<sup>a</sup> The angular position of Pt(220) reflection peak.

<sup>b</sup> Lattice parameter and Pt–Pt bond distance calculated from XRD measurements.

<sup>c</sup> Crystallite sizes of the Pt-based catalysts calculated by line broadening of powder XRD peak at around  $68^\circ$  using the Scherrer equation.

<sup>d</sup> Mean particle diameter of the Pt-based catalyst from TEM images using at least 100 visible particles.

<sup>e</sup> Relative % of the Pt<sup>0</sup> species.

<sup>f</sup> Relative % of the Pt<sup>2+</sup> species.

<sup>g</sup> Relative % of the Ru<sup>0</sup> species.

<sup>h</sup> Relative % of the Ru<sup>4+</sup> species.

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