# Supporting information

## Graphene-supported Pt and PtPd Nanorods with Enhanced Electrocatalytic Performance for Oxygen Reduction Reaction

Yi-Chia Tseng , Hong-Shuo Chen, Yu-Ting Liang, Tsan-Yao Chen, Chen-Wei Liu, Shu-Ru Chung, Chien-Te Hsieh, Cheng-En Lee, and Kuan-Wen Wang\*<sup>a</sup>,

\*To whom correspondence should be addressed, E-mail: kuanwen.wang@gmail.com Fax: 886-3-2805034, Tel: 886-3-4227151 ext 34906 Current address: Institute of Materials Science and Engineering, National Central University, No.300, Jhongda Rd., Taoyuan 32001, Taiwan.

#### **1. Experimental Procedure**

#### 1.1Preparation of Graphene

The procedure for preparing graphene oxide (GO) powders was based on a modified Hummers' method. First of all, 5 g natural graphite (NG) and 2.5 g NaNO<sub>3</sub> were poured into 115 mL concentrated H<sub>2</sub>SO<sub>4</sub>. The graphite slurry was then placed in an ice bath for 2 hr. After that, 15 g KMnO<sub>4</sub> was slowly added into the graphite slurry. After that, 30 vol% H<sub>2</sub>O<sub>2</sub> (15 mL) was poured into in the slurry until the color of the mixture tended to become dark yellow. The as-prepared GO powders was redispersed in distilled water, and 1 vol% HCl solution was added into the aqueous mixture for replacing  $SO_4^{2-}$  ions by Cl<sup>-</sup> ions. The graphene nanosheets (GN) powders were synthesized by chemically reducing the resulting GO powders. The GO slurry was chemically reduced under microwave irradiation, using a household microwave oven. The microwave power and reduction period were set at 720 W and 3 min, respectively. The microwave-assisted approach is capable of forming the dispersion of GNs in EG solution. After filtering, the GN powders were dried in a vacuum oven at 105°C overnight.

#### 1.2 Preparation of Carbon and Graphene-supported NRs

Carbon- and graphene-supported Pt and PtPd NRs with metal loading about 40 wt% were prepared by the formic acid method.  $H_2PtCl_6 \cdot 6H_2O$  and HCOOH were used as

received from Alfa Aesar. Carbon black (Vulcan XC-72) and graphene were used as supporting materials. First, 0.5 mg carbon black or graphene was dispersed in the solution by magnetic stirrer. The aqueous solutions of H<sub>2</sub>PtCl<sub>6</sub> were completely dissolved in deionized water. Afterwards, the solution of H<sub>2</sub>PtCl<sub>6</sub> and carbon or graphene were mixed and reduced by formic acid for 72 h. For the preparation of PtPd NRs with an atomic Pt/Pd ratio of 3/1, Pd(NO<sub>3</sub>)<sub>2</sub> was added and reduced by formic acid for another 48 h. The carbon supported Pt, carbon-supported PtPd, graphene supported Pt, and graphene-supported PtPd NRs were washed, dried, stored, and named as C-Pt, C-PtPd, G-Pt or G-PtPd NRs, respectively. Besides, the 0-dimentional (0-D) carbon-supported Pt NPs (Pt/C, 46% from TKK) was also used for comparison.

### 1.3 Characterization of Carbon and Graphene-supported NRs

The typical XAS spectra of various catalysts were obtained in fluorescence mode at the BL01C1 and 17C beamlines at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. A Si monochromator was employed to adequately select the energy with a resolution  $\Delta E/E$  better than 10<sup>-4</sup> at the Pt L<sub>II</sub> -edge (13273 eV), Pt L<sub>III</sub> -edge (11563 eV), and the Pd K-edge (24350 eV). All catalysts were dispersed uniformly on the tape and prepared as thin pellets with an appropriate absorption thickness ( $\mu$ x=1.0, where  $\mu$  is the X-ray attenuation coefficient at the absorption edge and x is the thickness of the sample) to attain a proper edge jump step at the absorption edge region. In order to acquire acceptable quality spectra with good quality, each measurement was repeated at least twice and averaged for successive comparison.

For the EXAFS analysis, the backgrounds of the pre-edge and the post-edge were subtracted and normalized with respect to the edge jump step from the XAS spectra. The normalized spectra were transformed from energy to k-space and further weighted by k<sup>3</sup> to distinguish the contributions of back scattering interferences from different coordination shells. Normally, the backscattered amplitude and phase shift functions for specific atom pairs were theoretically estimated by means of utilizing the FEFF7 code.

The  $H_{Ts}$  values are obtained from the Pt  $L_{II}$  and  $L_{III}$  white lines of XANES. The fractional change in Pt HTs relative to the reference material ( $f_d$ ) can be estimated: <sup>1</sup>

$$f_{d} = \frac{\left(\Delta A_{3} + 1.11\Delta A_{2}\right)}{(A_{3} + 1.11A_{2})r}$$
(1)

$$\Delta A_2 = (A_{2s} - A_{2r}) \text{ and } \Delta A_3 = (A_{3s} - A_{3r})$$
(2)

where  $A_2$  and  $A_3$  represent the areas under  $L_{II}$  and  $L_{III}$  absorption edges of the sample (s) and reference (r) material. The  $H_{Ts}$  value of Pt can be evaluated using the following equation:

$$H_{Ts} = (1+f_d) H_{Tr}$$
(3)

The electrochemical measurements were conducted using a CHI700a potentiostat and a classical electrochemical cell with a three-electrode configuration. 5 mg of electrocatalysts in isopropyl alcohol and Nafion solution (5 wt%, DuPont) were ultrasonically dispersed and dropped on a glass carbon electrode RDE (0.196 cm<sup>2</sup>). The metal loading on a RDE was about 20.1 µg for all catalysts in this work. The saturated calomel electrode and Pt plate was severed as the reference and counter electrode, respectively. A 0.5 M HClO<sub>4</sub> (Panreac) aqueous solution was used as the electrolyte, and saturated with highpurified O<sub>2</sub> at room temperature. All potentials in this study referred to normal hydrogen electrode (NHE). Oxygen reduction current of negative-going scans was measured by linear sweep voltammetry (LSV) with a scan rate of 5 mV s<sup>-1</sup> and a rotation rate of 1600 rpm. The Ik was calculated based on the following equation:

$$I_k = \frac{I_d I}{I_d - I} \tag{4}$$

where I,  $I_k$ , and  $I_d$  are the experimentally measured, mass transport free kinetic and diffusion-limited current density, respectively.

The ADT which were used to characterize the electrochemical stability and performance of the catalysts were obtained in the potential range of 0.6 to 1.20 V with the applied scan rate of 50 mV s<sup>-1</sup> under  $N_2$  atmosphere for 1000 cycles.

The LSV and cyclic voltammetry (CV) tests were performed every 200 scans under  $O_2$  and  $N_2$  atmospheres, respectively. Moreover, for Pt/C, C-Pt, and G-PtPd samples, the ADT conducted in  $O_2$  for 2000 cycles were also compared.

The CV can be applied to determine the ECSA of catalysts based on the hydrogen adsorption/desorption region. The CV tests were conducted from 0 to 1.20 V at a sweeping rate of 20 mV s<sup>-1</sup> under N<sub>2</sub> atmosphere. The ECSA was calculated by measuring the areas of H desorption between 0.05 and 0.4 V after the deduction of the double-layer region. By using the charge passed for H-desorption,  $Q_{\rm H}$ , the ECSA of Pt can be calculated using the following equation:<sup>2</sup>

$$ECSA = \frac{Q_H}{0.21}$$
(5)  
,where Q<sub>H</sub>, the

charge for H-desorption (mC/cm<sup>2</sup>); and 0.21, the charge required to oxidize a monolayer of  $H_2$  on clean Pt. For each catalyst, SA and MA were obtained when  $I_k$  was normalized to the ECSA and Pt loading, respectively.

The exact metal loadings of catalysts were determined by thermal gravimetric analysis (TGA, Perkin Elmer TGA-7). Initially, a small amount of catalysts was placed into a Pt basket with a temperature range from 323 to 1073 K and a heating rate of 10 K min<sup>-1</sup> under air atmosphere. The exact atomic

compositions of the alloy catalysts were examined by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Jarrell-Ash, ICAP 9000).

The phases and structures of the catalysts were characterized with a XRD using Cu K $\alpha$  radiation operated at 40 kV and 40 mA, and performed in a 20 range from 20 to 80° at a scan rate of 30 min<sup>-1</sup>. The morphologies of the catalysts were analyzed by HRTEM operated at a voltage of 200 kV. The XPS (Thermo VG Scientific Sigma Probe) using an Al K $\alpha$  radiation at a voltage of 20 kV and a current of 30 mA can be utilized to identify the surface compositions and oxidation states of the catalysts.

- 1. S. Mukerjee, S. Srinivasan, M. P. Soriaga and J. McBreen, *J. Electrochem. Soc.*, **1995**, *142*, 1409.
- 2. A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, L. Giorgi, J. Power Sources 2002, 105, 13.



Figure S1 HRTEM images for the as-prepared (a) G-Pt, (b) C-PtPd, (c) G-Pt, and (d) C-PtPd catalysts after ADT.



Figure S2 XRD patterns of Pt/C, C-Pt, C-PtPd, G-Pt, and G-PtPd catalysts.



Figure S3 The EXAFS spectra and fitting results of C-PtPd and G-PtPd for the Pd K-edge.

2.73

2.74

2.09

-2.69

0.001

Pd-Pt

Pd-Pd

1.60

2.90



Sample	shell	Ν	R[A]	$\sigma^{2}(x10^{-3})$	$\Delta E_0$	R factor
				[Å <sup>2</sup> ]	[eV]	
C-Pt	Pt-O	1.02	1.99	5 60	8.62	0.001
	Pt-Pt	6.68	2.76	5.09		
G-Pt	Pt-O	0.62	2.00	5 60	7.54	0.001
	Pt-Pt	6.82	2.75	5.09		
C-Pt3Pd	Pt-O	0.59	1.97	5 60	7.01	0.001
	Pt-Pt	7.57	2.75	5.09		
G-Pt3Pd	Pt-O	0.28	1.98	5 (0	7.00	0.004
	Pt-Pt	7.34	2.75	3.09		

Figure S4 The EXAFS spectra and fitting results of C-Pt, C-PtPd, G-Pt, and G-PtPd for the Pt L3-edge.

samples	(111)	(200)	(220)	(111)+(220)/(200 )
Pt/C	1621	757	352	2.606
C-Pt	2756	1466	1157	2.669
G-Pt	1201	561	407	2.866
C-PtPd	2182	947	583	2.920
G-PtPd	1408	502	378	3.558

Table S1 The data analyses of XRD patterns of Pt/C, C-Pt, C-PtPd, G-Pt, and G-PtPd NRs.



Figure S5 The XANES spectra at the Pt  $L_{\rm III}$  edge for Pt/C, C-Pt, C-PtPd, G-Pt, and G-PtPd catalysts.

Catalysts	H <sub>Ts</sub>	I <sub>0.85</sub>	I <sub>0.85-1000</sub>	ECSA	MA	MA <sub>1000</sub>	SA	SA1000	MA1000/MA
		mA/cm <sup>2</sup>		$(m^2/g)$	(mA /mg <sub>Pt</sub> )		$(mA/cm^2_{H Charge})$		(%)
Pt/C	0.338	3.26	2.02	55.7	74.3	46.0	0.13	0.08	62
C-Pt	0.314	3.69	3.25	43.3	114.5	101.1	0.27	0.24	88
G-Pt	0.307	4.21	3.95	38.6	117.6	107.5	0.30	0.27	91
C-PtPd	0.306	4.35	3.30	42.3	133.2	101.0	0.32	0.24	76
G-PtPd	0.295	4.92	4.26	23.6	142.4	123.3	0.60	0.52	87

Table S2 The  $H_{Ts}$ ,  $I_k$ , ECSA, MA, SA, and MA retention of Pt/C, C-Pt, C-PtPd, G-Pt, and G-PtPd catalysts.



Figure S6 TGA results of C-Pt,G-Pt, C-PtPd, and G-PtPd catalysts and the exact Pt loadings of PtPd NRs measured by ICP.



Figure S7 SA changes of Pt/C, C-Pt, and G-PtPd in  $O_2$  during 2000 cycles of ADT.



Figure S8 XPS spectra of Pt/C, C-Pt,G-Pt, C-PtPd, and G-PtPd catalysts.