# **Supporting Information**

### Rh nanoparticles supported on ultrathin carbon nanosheets for

## high-performance oxygen reduction reaction and catalytic hydrogenation

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#### **Experimental**

### **1. Material and Materials Preparation**

### **1.1 Materials**

Rhodium chloride trihydrate (RhCl<sub>3</sub>·3H<sub>2</sub>O, Rh $\geq$  39wt%, Northwest Institute For Non-ferrous Metal Research, Xi'An Catalyst Chemical Co., Ltd), <u>sodium sulfate</u> (Na<sub>2</sub>SO<sub>4</sub>, AR, Shanghai Chemical Reagent Co., Ltd ), <u>sodium oleate</u> (CR, Tianjin Kemiou Chemical Reagent Co., Ltd.), absolute ethanol (>99.7%, Sinopharm Chemical Reagent Co., Ltd), <u>potassium hydroxide</u> (KOH, AR, Sinopharm Chemical Reagent Co., Ltd), <u>potassium hydroxide</u> (KOH, AR, Sinopharm Chemical Reagent Co., Ltd), commercial Rh/C (10 wt%, Alfa Aesar), commercial Pt/C (20 wt%, Sigma-Aldrich). All reagents were used as received without purification and water was deionized immediately before use in a Millipore Direct-Q system (18.2 M $\Omega$  cm).

### **1.2. Materials Preparation**

### 1.2. Preparation of Rh/C nanosheets

Firstly, to obtain Rh/C nanosheets, rhodium oleate was synthesized in advance. In a typical synthesis process, 263.3 mg RhCl<sub>3</sub>·3H<sub>2</sub>O was dissolved in 3 mL deionized  $H_2O$  (rose madder), afterwards 1.22 g sodium oleate was added slowly into this

solution. After that, the mixture was heated at 90 °C for 2 h. After converting completely, 10 g Na<sub>2</sub>SO<sub>4</sub> was added slowly into the resulting yellow slurry under vigorous stirring. In the subsequent baking for 2 h, the damp-dry slurry was transformed to corundum crucible and calcined at 500 °C for 3 h in the tube furnace under N<sub>2</sub> atmosphere. At the end of calcination process, the black solids were washed with hot water and centrifuged several times to remove the Na<sub>2</sub>SO<sub>4</sub> template. At last, the collected Rh/C nanosheets were dried at 60 °C in a drying oven for further use. As control experimental, the heat treatment at 800 °C or without Na<sub>2</sub>SO<sub>4</sub> template had been carried out under the same condition.

### 2. Materials Characterization

Scanning electron microscopy (SEM) was measured on a Quanta 400 FEG field-emission scanning electron microscope. Transmission electron microscopy (TEM) was measured on a Tecnai G2 F20 S-Twin field-emission transmission electron microscope.. Atomic force microscopy (AFM) analysis was performed on a Bruker Dimension Icon atomic force microscope. X-ray diffraction (XRD) was collected on a Bruke D8. Raman analysis was performed on a Renishaw Invia using a 514 nm laser irradiation.TG analysis was performed on Netzsch STA 449C. BET analysis was carried out on TriStarII3020. Electrochemical measurements were performed by an Autolab PGSTAT302N.

### 3. Electrochemical Measurements

For the preparation of catalyst inks, 5 mg Rh/C nanosheets, 20 wt% commercial Pt/C, 10 wt% commercial Rh/C were disperse in 0.95 mL absolute ethanol, respectively. Furthermore, at least 30 min of sonication was needed to form homogeneous inks. Afterwards, 50  $\mu$ L 5 wt% Nafion solution was added and ultrasonic the inks for another 30 min. Then, 4  $\mu$ L of catalyst inks (containing 20  $\mu$ g of catalyst) were loaded on glass carbon electrode with 3 mm diameter (0.07065 cm<sup>2</sup>). The mass loading of catalyst was ~0.28 mg/cm<sup>2</sup>. All ORR measurements were performed in an electrochemical cell with a platinum plate as counter electrode, a Ag/AgCl electrode filled with 3 M KCl as the reference electrode, and the catalysts-modified glass carbon rotating disk electrode (RDE) as the working electrode. At the start of each experiment, the electrolyte (0.1 M KOH) was saturated

with oxygen by a flow of O<sub>2</sub>. To be noted, the flow of O<sub>2</sub> was maintained throughout the entire tests to ensure its continuous O<sub>2</sub> saturation. Linear sweep voltammetry (LSV) was cathodically scanned at 5 mV/s with different rotating speeds, from 400 rpm to 2500 rpm. Cyclic voltammetry (CV) was conducted at a rate of 50 mV/s with Ar saturated electrolyte. All polarization curves were corrected with Ar and *iR*-compensation, which are given versus reversible hydrogen electrode (RHE) according to  $E_{vs. RHE} = E_{vs. Ag/AgCl} + E^{\theta}Ag/AgCl + 0.0591$  pH.

# 4. UV-vis Absorption Spectrum Measurements of 4-nitrophenol

The UV-vis absorption spectra of 4-nitrophenol (4-NP) in the presence of NaBH<sub>4</sub> were monitored using a Shimadzu UV-1700 spectrophotometer over the wavelength range from 300 to 600 nm. The process was carried out in a well-stoppered quartz cuvette. In a typical process, 0.2 ml of the Rh/C catalysts dispersion (0.1mg/mL) was added to 2 ml of 4-NP stock solution (0.0625 mM). Then 1 ml of freshly prepared NaBH<sub>4</sub> aqueous solution (0.125 M) was added to the above solution and UV-visible absorption spectra were monitored at different time intervals.



**Supplemental Figures** 

**Figure S1**. FT-IR spectra of the  $RhCl_3$  (black curve), sodium oleate (red curve) and rhodium oleate complex (blue curve), respectively.



Figure S2. SEM image of Rh/C-500 nanosheets.



Figure S3. SEM image of Rh/C-500 obtained from the heat treatment without  $Na_2SO_4$ .



Figure S4. SEM image of Na<sub>2</sub>SO<sub>4</sub>.



Figure S5. Element mappings of Rh/C-500 nanosheets.



**Figure S6.** a) TEM image of commercial Pt/C; b) is corresponding particle size distribution. The average size of Rh NPs is  $\sim 4.4$  nm.



**Figure S7.** low resolution (a) and high resolution (b) TEM image of commercial Rh/C, respectively; The inset in b) is corresponding particle size distribution. The average size of Rh NPs is ~ 4 nm.



**Figure S8.** low resolution (a) and high resolution (b) TEM image of Rh/C-500 nanosheets obtained from the heat treatment without Na<sub>2</sub>SO4; The inset in b) is corresponding particle size distribution. The average size of Rh NPs is ~ 6.7 nm.



Figure S9. a) AFM images of Rh/C-500 nanosheets.



Figure S10. TG plot of commercial Pt/C, commercial Rh/C and Rh/C-500 nanosheets.



**Figure S11**. a), c) and e) are  $N_2$  adsorption–desorption isotherms of commercial Pt/C, commercial Rh/C and Rh/C-500 nanosheets, respectively. b), d) and f) show corresponding pore size distributions of commercial Pt/C, commercial Rh/C and Rh/C-500 nanosheets, respectively.



Figure S12. SEM images of Rh/C-800 nanosheets.



**Figure S13**. a) and b) are low resolution and high resolution TEM images of Rh/C-800 nanosheets, respectively. It is obvious that the size of Rh NPs changes to bigger. The average size of Rh NPs is  $\sim 5$  nm.



Figure S14. a) is  $N_2$  adsorption–desorption isotherms of Rh/C-800 nanosheets and b) shows its corresponding pore size distribution.



Figure S15. a) XRD plot of Rh/C-800 nanosheets; b) Raman spectrum of Rh/C-500 nanosheets and Rh/C-800 nanosheets and the corresponding  $I_D/I_G$  are 1.05 and 0.92, respectively.



Figure S16. TG plot of c Rh/C-800 nanosheets.



**Figure S17.** a) LSV of Rh/C-800 nanosheets in  $O_2$ -saturated 0.1 M KOH electrolytes at a scan rate of 5 mV/s with 1600 rpms rotating speed; b) Chronopotentiometric response (percentage of current versus operation time) of Rh/C-800 nanosheets at 0.7 V versus RHE in  $O_2$ -saturated 0.1 M KOH electrolytes, respectively.



**Figure S18**. LSV of Rh/C-500 obtained from the heat treatment at 500  $^{\circ}$ C without Na<sub>2</sub>SO<sub>4</sub> in O<sub>2</sub>-saturated 0.1 M KOH electrolytes at a scan rate of 5 mV/s with 1600 rpms rotating speed.



**Figure S19**. LSV Plots of Rh/C-500 nanosheets calcinated at O<sub>2</sub> atmosphere (1), Rh/C-500 which exposed in the air for 2 months (2), and freshly prepared Rh/C-500 nanosheets (3). To investigate the influence of Rh oxide on catalytic performance (see M. E. Grass, Y. Zhang, D. R. Butcher, J. Y. Park, Y. Li, H. Bluhm, K. M. Bratlie, T. Zhang, and Gabor A. Somorjai, *Angew. Chem. Int. Ed.* 2008, **47**, 8893–8896; S. M. Kim, K. Qadir, B. Seo, H. Y. Jeong, S. H. Joo, O. Terasaki and J. Y. Park, *Catal. Lett.* 2013, **143**, 1153–1161.), a control experiment has been done where three kinds of Rh nanoparticles with different oxidation degree were synthesized. It shows that the freshly prepared Rh/C-500 nanosheets deliver the optimal ORR performance. The Rh/C-500 nanosheets calcinated at O<sub>2</sub> atmosphere deliver the worst ORR performance among the three catalysts. Our results indicate that too much oxidation of Rh decrease the ORR performance of Rh.



**Figure S20**. UV-vis absorption spectra of 4-NP in the presence of Rh/C-500 nanosheets at the end of the hydrogenation.



**Figure S21.** a) and c) are UV-vis absorbance spectra of -NP by NaBH<sub>4</sub> in the absence of Rh/C catalyst and in the presence of Rh/C-800 nanoshees; b) and d) are corresponding logarithm of the absorbance at 400 nm vs. reduction time.