*Eelctornic Supplementary Information*

# Enhancement of the electrocatalytic activity of Pt nanoparticles in oxygen reduction by chlorophenyl functionalization

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## 1. Reagents and materials

Platinum chloride ($PtCl_2$, 73% Pt, ACROS), 4-chloroaniline (97%, Aldrich), sodium borohydride ($NaBH_4$, 98%, ACROS), sodium nitrite ($NaNO_2$, 98%, ACROS), perchloric acid ($HClO_4$, 70 wt%, ACROS), toluene (HPLC grade, Fisher Scientific), tetrahydrofuran (THF, HPLC grade, Fisher Scientific), and high purity $O_2$ (99.993%, Praxair Inc.) were used as received. A commercial Pt/C catalyst was purchased from Alfa Aesar (20 *wt*.%, HiSPEC$^{TM}$3000, Johnson Matthey). Water was supplied by a Barnstead Nanopure water system (18.3 MΩ·cm).

## 2. Synthesis of chlorophenyl-stabilized Pt (Pt-ArCl) nanoparticles

$PtCl_2$ (26.6 mg, 0.1 mmol) was dissolved in hydrochloric acid (~2 mL) under heating. After most of hydrochloric acid was evaporated, the product of $H_2PtCl_4$ was dissolved in water (~1 mL), and cooled in an ice-water bath. Chlorophenyl diazonium was synthesized by the following procedure: To a beaker was added a $HClO_4$ solution (35%, 0.45 mL), 4-chloroaniline (63.8 mg, 0.5 mmol) and THF (0.5 ml). Under magnetic stirring and cooled in an ice-water bath, to the solution was added dropwise a cooled $NaNO_2$ (35 mg, 0.5 mmol) solution to produce the diazonium salt. After about 20 min, to the diazonium solution was added above ice-cooled $H_2PtCl_4$ solution and $H_2O$-THF (v:v = 1:1, 20 mL) mixture solvent. In this mixture solvent, both the diazonium and final product (i.e., Pt-ArCl) are soluble. Under magnetic stirring, $NaBH_4$ solution (0.2 M, 3 mL) was then added dropwise to the above yellow solution. The solution color changed gradually from yellow to dark brown, indicating the formation of Pt nanoparticles. Subsequently, the nanoparticles was extracted by toluene (20 mL), and washed with 0.1 M $H_2SO_4$ solution and water several times. After most of the solvent was rotary evaporated, the Pt-ArCl nanoparticles were precipitated by hexane, which were then collected by centrifugation and further washed four times with ethanol-hexane (1:5) to remove impurities and excessive free ligands. Finally, the purified Pt-AtCl nanoparticles were dissolved in ethanol.

## 3. Modification of Pt/C with chlorophenyl group (Pt/C$^{ArCl}$)

Commercial Pt/C catalyst (80 mg) was ultrasonically dispersed in THF-$H_2O$ (v:v = 1:1, 40 mL). To this dispersion was added chlorophenyl diazonium salt (0.5 mmol). Under magnetic stirring and cooled in an ice-water bath, $NaBH_4$ solution (0.2 M, 3 mL) was then added slowly to the above mixed solution to reduce diazonium salts. The generated aryl radicals may attach on the both Pt nanoparticles and carbon black. The Pt/C$^{ArCl}$ product was then extracted by toluene, and washed with 0.1 M $H_2SO_4$ solution and water several times. After most of the solvent was rotary evaporated, the Pt/C$^{ArCl}$ was further washed four times with THF-hexane (1:5) to remove impurities and excessive free ligands.

## 4. Electrochemistry

Electrochemical studies were carried out in a standard three-electrode cell connected to a CHI-440 (CHI-710 bipotentiostat for RRDE) electrochemical workstation, with a Pt foil counter electrode and a reversible hydrogen electrode (RHE) at room temperature (~20 ºC). Two working electrodes purchased from Pine Inc. are employed, i.e., a rotating disk electrode (RDE, #AFE2M050GC, glassy carbon (GC), $\phi$ = 5 mm) and a rotating ring-disk electrode (RRDE, #AFE7R9GCAU, GC ($\phi$ = 5.61 mm) disk and Au ring). The collection efficiency was determined to be 37.3% by RRDE measurements in 5 mM $K_4Fe(CN)_6$ + 0.1 M $Sr(NO_3)_2$, which is very close to the manufacturer's value of 37%.

An ethanolic solution of Pt-ArCl nanoparticles was mixed with XC-72 carbon black and Nafion 117 solution (5 wt %, Fluka) to form a well dispersed catalyst "ink" (Pt : C = 1:4 (w:w), Pt concentration: 0.20 mg $mL^{-1}$, Nafion: 0.05%) under ultrasound. Similarly, the commercial Pt/C and $Pt/C^{ArCl}$ were also dispersed in ethanol to form a catalyst ink containing 0.20 $mg_{Pt}$ $mL^{-1}$. To prepare the working electrode, a calculated amount of the catalyst inks was dropcast onto the polished glassy carbon. The Pt loading on the glassy carbon electrodes was 10 μg $cm^{-2}$ in all cases. As soon as the electrode was dried in air, a dilute Nafion solution (0.1 wt.%, 3μL) was added onto it.

The electrocatalytic activity for oxygen reduction reaction (ORR) was tested in an $O_2$-saturated 0.1 M $HClO_4$ with a rotating disk electrode system (Pine Inc.) at a rotation rate of 1600 rpm. Electrode potential was scanned from +0.05 to +1.30 V at 10 mV $s^{-1}$, and the solution ohmic drop (i.e., IR drop) was electronically compensated.

## 5. Thermogravimetric analysis (TGA)

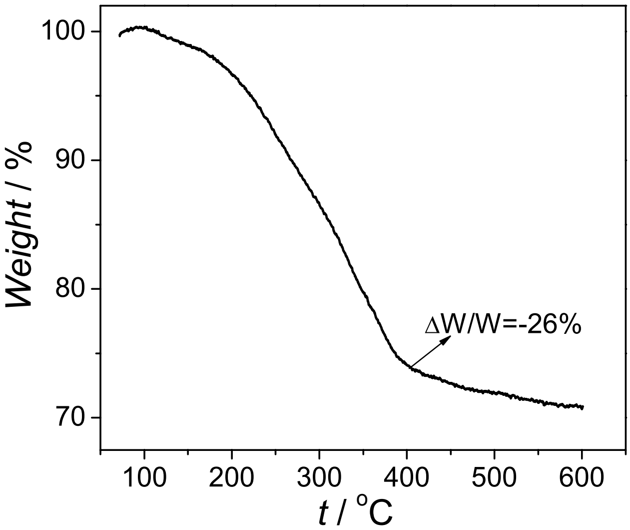

**Figure S1.** TGA curve of Pt-ArCl nanoparticles measured under a $N_2$ atmosphere at a heating rate of 10 ºC $min^{-1}$. The considerable mass loss appears at over 200 °C. The amount of organic content on the nanoparticles is about 26%. On the basis of the weight loss and the average core size (1.85 nm) of the Pt nanoparticles, we can estimate that the average area occupied by one chlorophenyl ligand is about 8 Å$^2$. This value is considerably lower than the typical value (~20 Å$^2$) for long-chain alkanethiolates adsorbed on metal nanoparticles,[1] but is consistent with that of decylphenyl-stabilized Pt nanoparticles (~5.5 Å$^2$) reported previously.[2] Clearly, such a small footprint of the aryl group on Pt suggests that the ligands likely formed a multilayer structures on the nanoparticle surface.[3, 4]

[1] M. J. Hostetler, J. E. Wingate, C. J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J.

Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans, and R. W. Murray, *Langmuir*, 1998, **14**, 17.

[2] F. Mirkhalaf, J. Paprotny, and D. J. Schiffrin, *Journal of the American Chemical Society*, 2006, **128**, 7400.

[3] A. Adenier, C. Combellas, F. Kanoufi, J. Pinson, and F. I. Podvorica, *Chemistry of Materials*, 2006, **18**, 2021.

[4] J. K. Kariuki and M. T. McDermott, *Langmuir*, 1999, **15**, 6534.

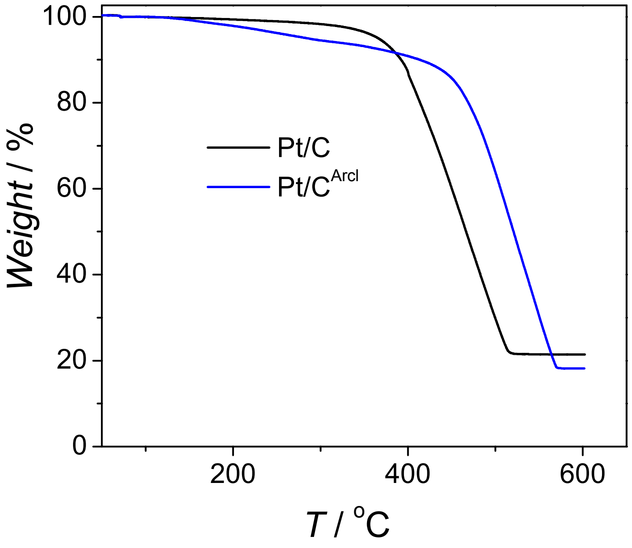

**Figure S2.** TGA curve of the Pt/C and Pt/C$^{ArCl}$ nanoparticles measured under a $N_2$ atmosphere at a heating rate of 10 ºC min$^{-1}$. The carbon black support was burned out due to the trace $O_2$ in $N_2$ gas at temperature higher than 400 °C. Clearly, the Pt/C$^{ArCl}$ shows more weight loss between 200 and 400 °C. This weight loss (~ 10%) may be attributed to the chlorophenyl group on the Pt/C surface.

## 6. TEM images and size histogram of Pt/C

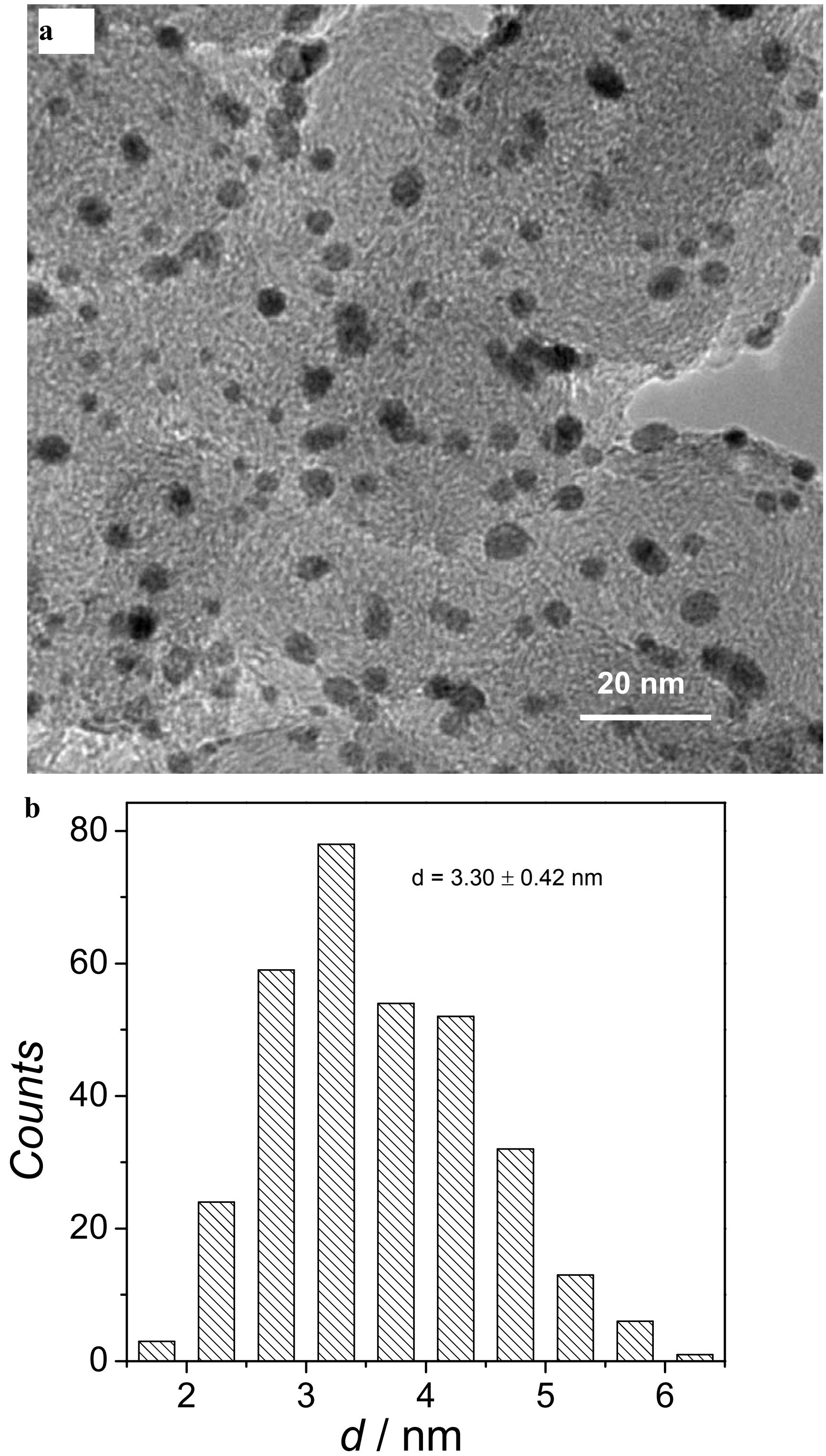

**Figure S3.** (a) TEM image and (b) size histogram of the commercial Pt/C catalysts.

## 7. Background current correction for ORR

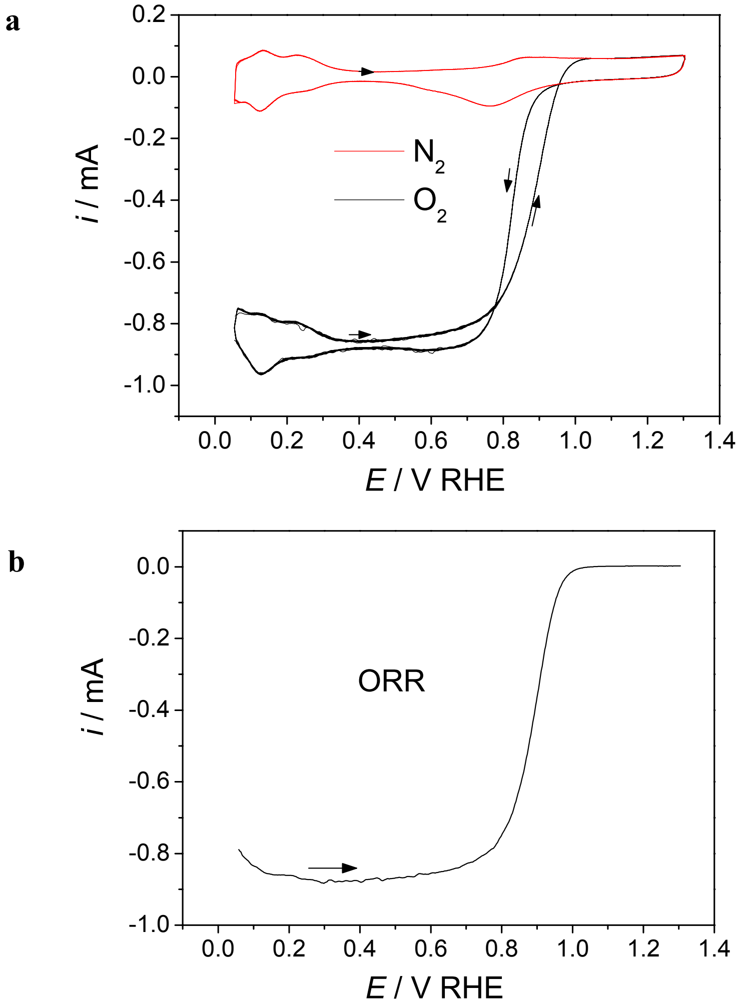

**Figure S4.** (a) Cyclic voltammograms of Pt-ArCl nanoparticles recorder in $N_2$-saturated and $O_2$-saturated 0.1 M $HClO_4$ solution at 50 mV $s^{-1}$. Rotating rate: 900 rpm. (b) Forward-scan ORR polarization curve after background current correction. Black lines in Figure S4 (a) are the typical cyclic voltammograms of the Pt-ArCl nanoparticles under the durability test of continuous potential cycling in $O_2$-saturated 0.1 M $HClO_4$ solution. Clearly, at the scan rate of 50 mV $s^{-1}$, the background currents from adsorption/desorption of hydrogen and oxygen, as well as double-layer charging (Red lines) can interfere the determination of ORR activity. To obtain the net ORR current, the CV curve recorded in $N_2$-saturated solution was subtracted from that recorded in $O_2$-saturated solution, resulting in the ORR polarization curve shown in Figure S4 (b).