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Supplementary Information

Exploring the Size Effects of Reduced Graphene Oxide Nanosheets for Pt-Catalyzed Electrode Reactions

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Experimental section

Synthesis of GO. GO was synthesized through the modified Hummers method which is one of the wet-chemical procedure using the graphite as the raw materials. First, as a pre-oxidation step, potassium persulfate ($K_2S_2O_8$, 2.5 g) and phosphorus pentoxide (P_2O_5, 2.5 g) were completely dissolved in sulfuric acid (H_2SO_4, 100 ml). After increasing the temperature up to 80 °C, the graphite powder (5 g) was added to the oxidizing mixture and kept for 30 min under vigorous stirring. The resulting solution was cooled to room temperature and kept for 12 h under stirring. The mixture solution was diluted with de-ionized water (DIW, 400 ml) and filtered several times with DIW until the pH of solution was close to that of DIW. The resulting pre-oxidized graphite was dried in 70 °C convection oven for 12 h. In the second oxidation step, the pre-oxidized graphite (2.5 g) was mixed with sulfuric acid (H_2SO_4, 250 ml) at 0 °C under vigorous stirring and kept for 45 min, then potassium permanganate ($KMnO_4$, 15 g) was added into the mixture solution. In this step, it is important to keep the solution temperature below 20 °C. The mixture solution was heated to 35 °C, and kept for 2 h with the ultrasonication (135 W, Branson Co.). After the solution diluted with the DIW (230 ml), 30% hydrogen peroxide aqueous solution (DIW, 700 ml + H_2O_2, 12 ml) was added, and obtained solution was centrifuged and washed with 37% hydrochloric acid (HCl, 380 ml) and DIW (1140 ml) mixture solution. The same procedure was repeated with the DIW until the pH value of solution becomes neutral. For removal of residual salts and ions, the product solution was treated with dialysis by using dialysis tubing cellulose membrane for 2 weeks. After that, un-exfoliated graphite oxide was removed through low rpm centrifugation treatment (1000 rpm, 2 min).

Size fractionation of GO sheets. The prepared GO sheets were separated with respect to its lateral size by pH induced selective sedimentation procedure. First, the pH of fresh GOcontaining aqueous solution was adjusted to pH4, and it was kept for 4 h in room temperature. The precipitated GO sheets are L-GO, and after the centrifugation of the residual supernatant (3500 rpm, 30 min), the small size GO sheets (S-GO) were produced. Size selected GO sheets were dried in freezing dryer for 2 days.

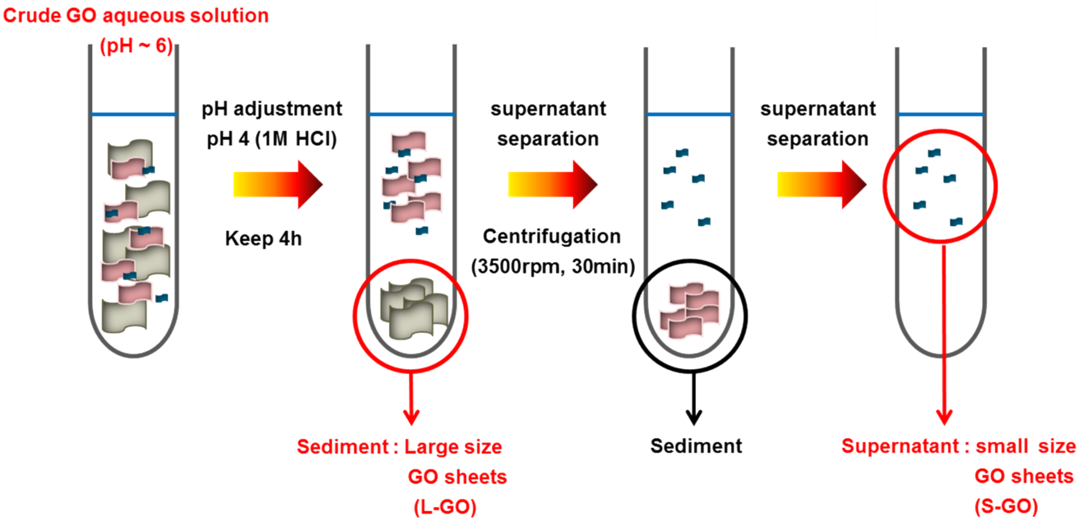

Fig. S1. The schematic illustration of GO size fractionation procedure

Synthesis of Pt/RGO catalysts. The Pt/RGO catalysts were synthesized via simultaneous chemical reduction of GO and Pt precursor in solution phase. The chloroplatinic acid hydrate ($H_2PtCl_6{\cdot}xH_2O$, 0.0118 g) as a Pt salt was dissolved in ethylene glycol ($HOCH_2CH_2OH$, 28.125 ml) which could play as reducing agent and solvent. Then, the pH of mixture solution was adjusted to 10 by using 1M sodium hydroxide (NaOH) solution. After that, the GO (0.0225 g) was dissolved in mixture solution under ultrasonication (135 W) for 1h. For the co-reduction from Pt precursor and GO to Pt metal and RGO, respectively, the mixture solution was subjected to 120 °C heat treatment for 24 h. After the product solution cooled to room temperature, it was washed by acetone (CH_3COCH_3) and DIW several times through the centrifugation at 3500 rpm for 10 min. The precipitated final product (Pt/RGO) was dried in freezing dryer.

Physicochemical characterization. The properties of GO and Pt/RGO were confirmed by several analysis equipment. The crystallographic structures were studied by X-ray diffractometer (XRD, Rigaku Ru-200B) using Cu K_α (λ= 1.5405 Å) source with a Ni filter and operating at 40 kV and 100 mA. The 2θ angular region between 5° and 70° (or 90° in case of Pt/RGO) was explored at a fixed time mode ($0.02° \ s^{-1}$). The morphologies were confirmed by field emission scanning electron microscope (FE-SEM, JEOL 7300) operated at 5 kV and 20 μA. Transmission electron microscope (TEM, Technai G2 S-Twin) operated at 300 keV, was also used for investigating the Pt/RGO catalysts. The chemical bonding states and surface compositions were confirmed by X-ray photo-electron spectroscopy (XPS, MULTILAB 2000 SYSTEM, SSK) with a monochromic Al K_α (E= 1486.6 eV). The composition of Pt/RGO was analyzed by thermogravimetric analysis (TGA, TGA-50H, Shimadzu), at condition of heating rate of 10 °C min^{-1} up to 900 °C in air atmosphere.

Electrochemical measurements of Pt/RGO catalysts.

The three-electrode cell consists of working electrode, counter electrode, and reference electrode, in which the glassy carbon electrode (GCE), Pt wire, and Ag/AgCl (3M KCl) were used, respectively, at room temperature. The working electrode was polished by 1, 0.3, 0.05 μm alumina paste to make the glassy carbon surface mirror like. To make the catalyst ink, Pt/RGO and 10wt% Nafion® ionomer solution were added into an aqueous solution of 50% isopropyl alcohol (IPA, $(CH_3)_2CHOH$, Fisher Chemical), and subjected to ultrasonication for 25 min. Electrocatalytic performances for the MOR were evaluated by three-electrode system with 0.07 cm^2 GCE, and the metal loading on GCE was 40 $\mu g \ cm^{-2}$. CV measurements was conducted over a potential range from -0.2 to 1.0 vs. Ag/AgCl in N_2-saturated 0.5 M H_2SO_4 and 0.5 M H_2SO_4 + 2.0 M CH_3OH electrolyte solutions at a scan rate of 50 mV s^{-1}. EIS using N_2-saturated 0.5 M H_2SO_4 + 2.0 M CH_3OH electrolyte over the frequency range of 10 kHz to 0.07 Hz at a constant voltage of 0.4 V vs. Ag/AgCl and cycling test with N_2-saturated 0.5 M H_2SO_4 + 2.0 M CH_3OH electrolyte for 300 cycles were also carried out. For the ORR analysis, 25 µg cm^{-2} of Pt was loaded on the 0.196 cm^2 GCE, in which was included the rotating disk electrode (RDE) system. To obtain the ORR polarization curves, linear sweep voltammetry (LSV) was conducted in O_2-saturated 0.1 M $HClO_4$ electrolyte at a scan rate of 10mV s^{-1} and rotation rate of 400, 900, 1600, and 2500 rpm. The accelerated durability test (ADT) was carried out by CV in N_2-saturated 0.1 M $HClO_4$ electrolyte solutions at a scan rate of 50 mV s^{-1} for 5000 cycles. All electrochemical characterizations in this work were conducted by Solartron Analytical instrument (AMETEK model 1470E cell test system), and all potentials were referenced to the reversible hydrogen electrode (RHE).

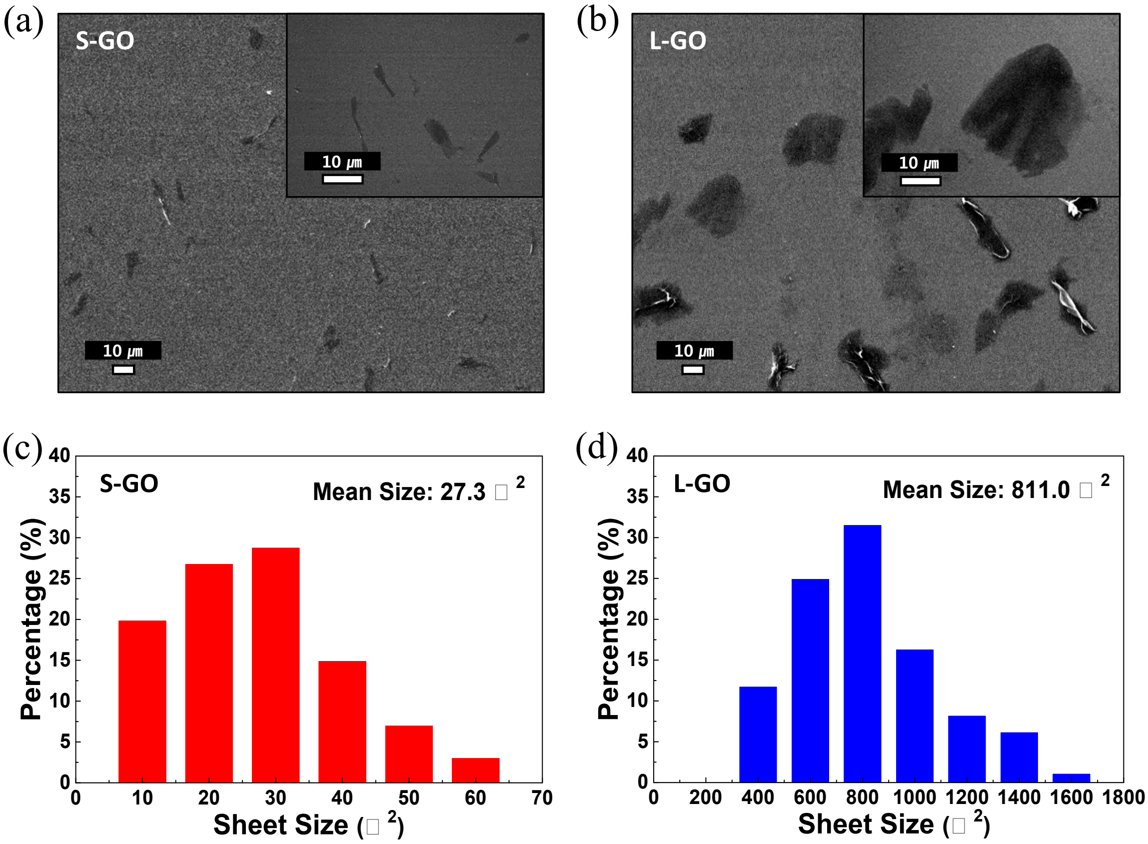

Fig. S2. The SEM images of (a) S-GO and (b) L-GO sheets on silanized Si substrate, and the histograms for sheets size distributions of (c) S-GO and (d) L-GO. The insets in SEM images show the magnified images.

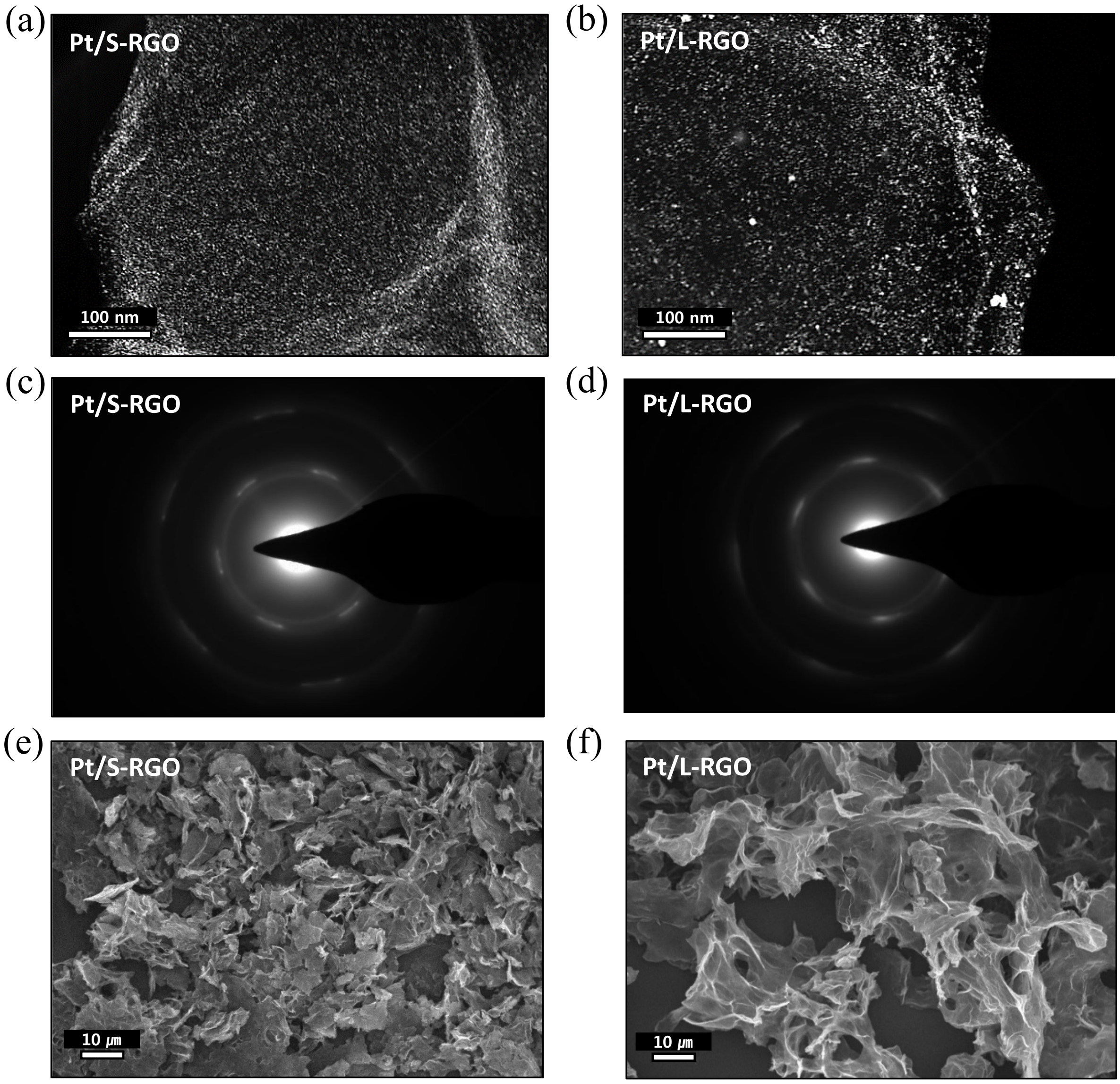

Fig. S3. (a) The dark field TEM image, (c) the TEM SAED patterns, and (e) the SEM image of Pt/S-RGO, and those (b, d, and f) for Pt/L-RGO, respectively.

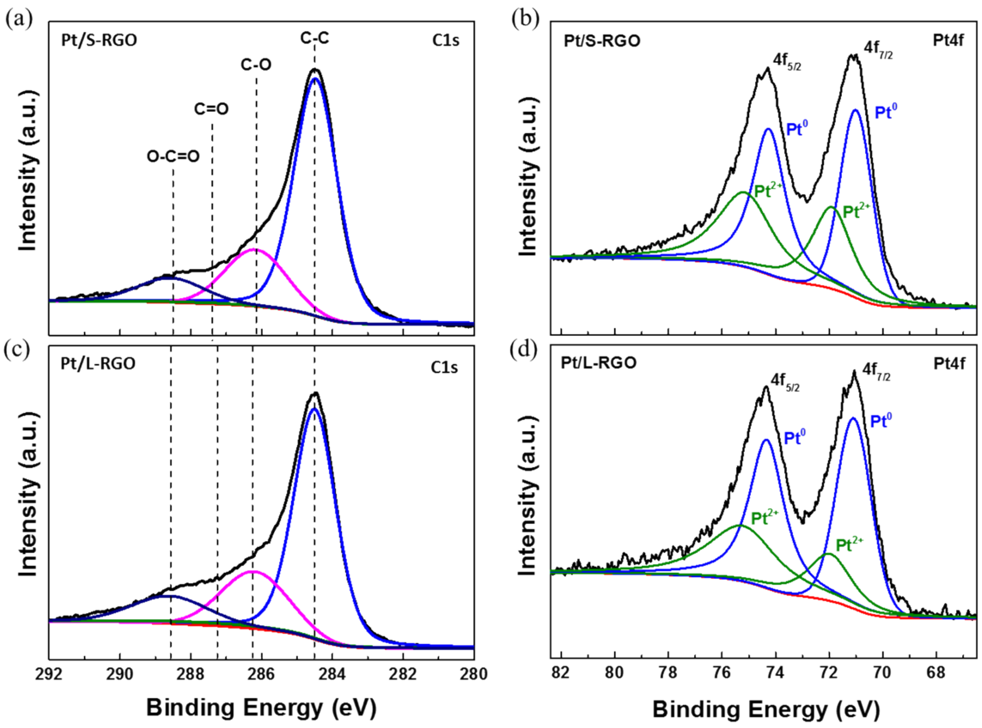

Fig. S4. The XPS spectra of Pt/S-RGO ((a) C1s and (b) Pt4f) and Pt/L-RGO ((c) C1s and (d) Pt4f).

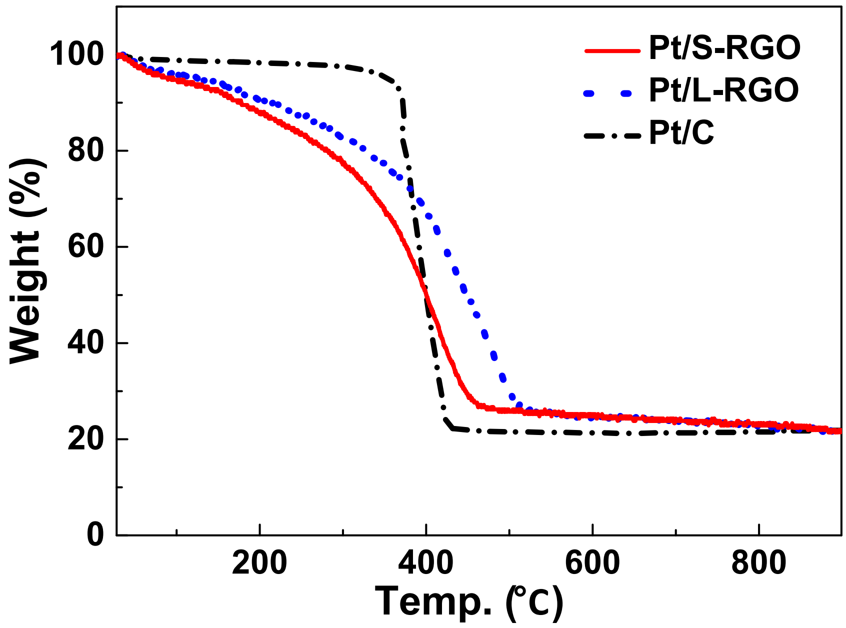

Fig. S5. The TGA results of Pt/S-RGO, Pt/L-RGO, and Pt/C catalysts.

Table S1. Electrochemical parameters of Pt/S-RGO, Pt/L-RGO, and Pt/C from the electrochemical analysis.

		MOR		ORR (at 0.85 V vs. RHE)		
Catalyst	ECSA (m^2 g^{-1})	Mass activity[a] j_m (mA $mg^{-1}{}_{Pt}$)	Specific activity[b] j_s (mA $cm^{-2}{}_{Pt}$)	Kinetic current density[c] j_k (mA cm^{-2})	Mass activity[d] j_m (mA $mg^{-1}{}_{Pt}$)	Specific activity[e] j_s (mA $cm^{-2}{}_{Pt}$)
Pt/S-RGO	65.6	315.3	0.481	0.85	34.1	0.052
Pt/L-RGO	44.5	215.4	0.484	0.65	24.9	0.056

[a] Forward anodic peak current normalized by the Pt mass.

[b] The activity normalized by the ECSA.

[c] Kinetic current normalized by the geometric surface area of electrode (0.196 cm^2).

[d] Kinetic current normalized by the Pt mass.

[e] The activity normalized by the ECSA.

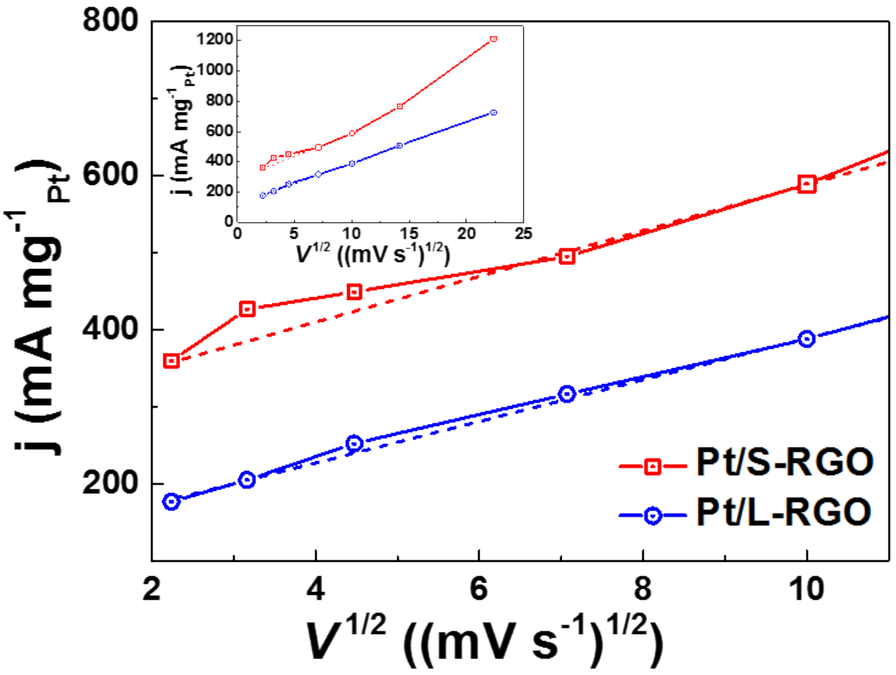

Fig. S6. The relationship between the mass activity and the square root of the scan rates (5, 10, 20, 50, 100, 200, and 500 mV s^{-1}) for the methanol oxidation reaction, and the inset shows the relationship over the entire range of scan rate.

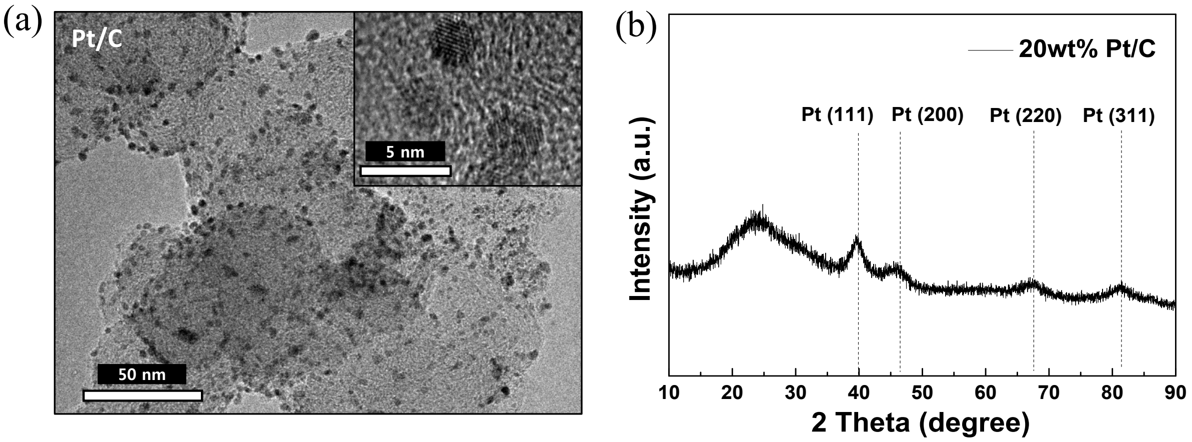

Fig. S7. (a) The bright field TEM image and (b) the XRD pattern of Pt/C.

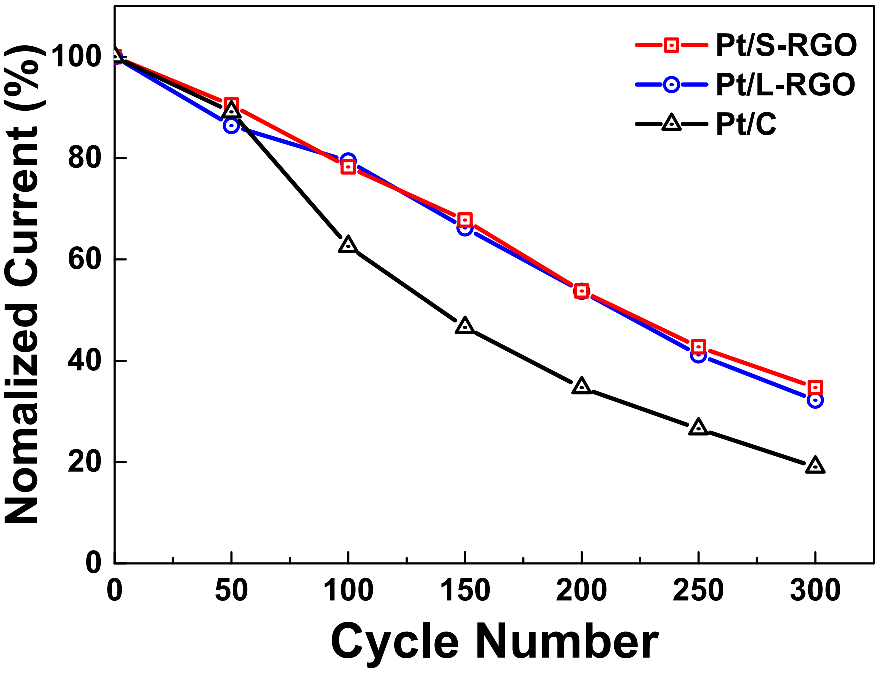

Fig. S8. The cycle data of the Pt/S-RGO, Pt/L-RGO, and Pt/C catalysts in N_2-saturated 0.5 M H_2SO_4 + 2.0 M CH_3OH electrolyte. The current was normalized by initial value.

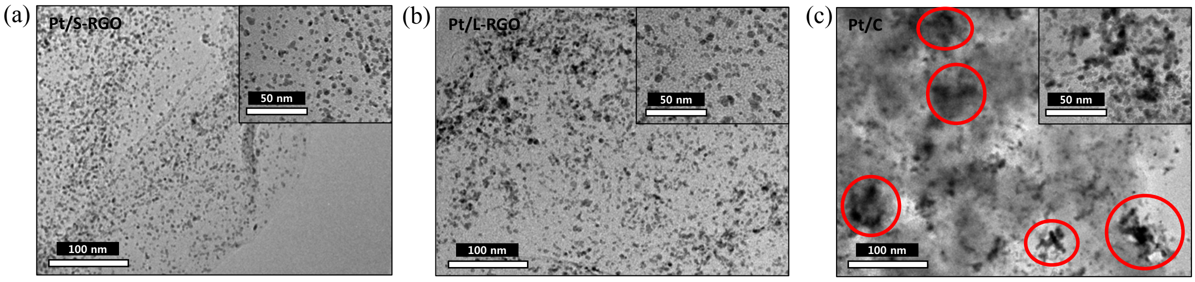

Fig. S9. The bright field TEM images of (a) Pt/S-RGO, (b) Pt/L-RGO, and (c) Pt/C after the 300 cycles of MOR.

The oxygenated functionalities on the RGO sheet serve the anchoring sites for loading of Pt nanoparticles and can give strong interaction between the RGO support and the metal nanoparticles, indicating that the Pt/RGO catalysts have higher long-term stability during the electrocatalytic reactions with higher resistance over sintering of Pt nanoparticles than the Pt/C. The Pt/C presented several significantly aggregated site (highlighted by red circle), whereas, the Pt/S-RGO and Pt/L-RGO revealed relatively high dispersion of Pt nanoparticles without serious agglomeration even after the reactions.

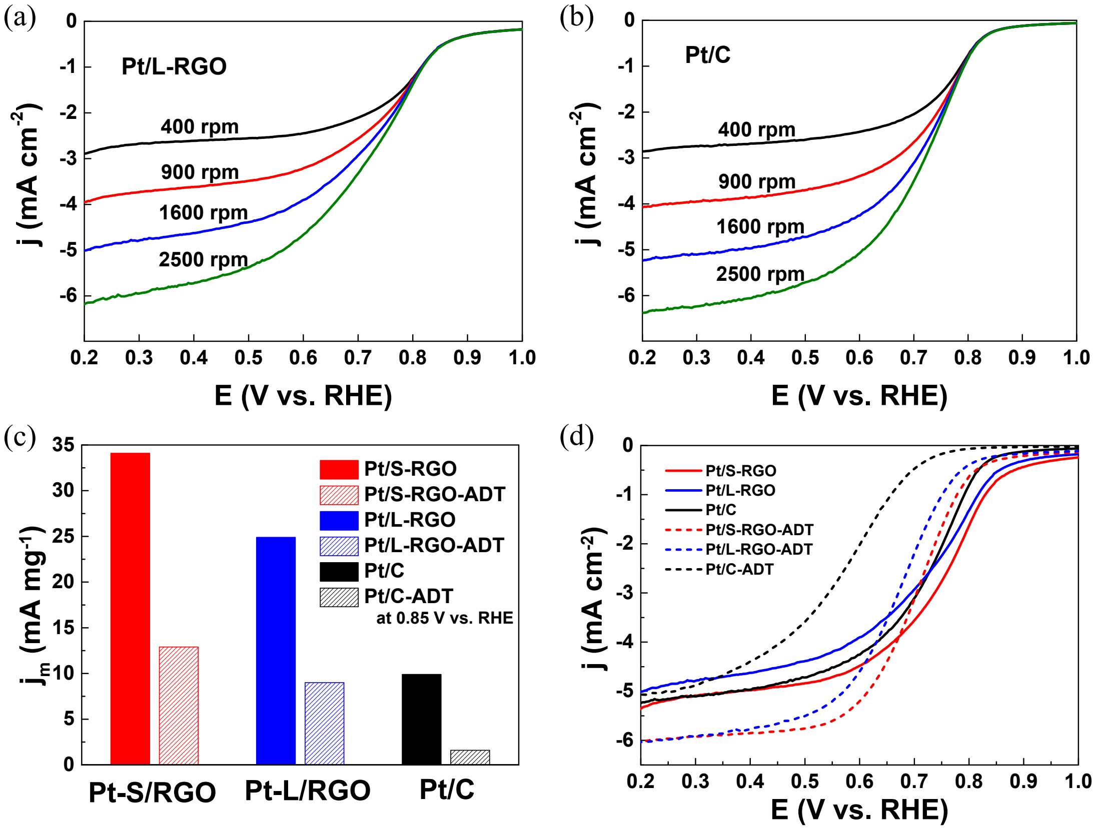

Fig. S10. ORR polarization curves of (a) Pt/L-RGO and (b) Pt/C catalysts at different rotation rates from 400 to 2500 rpm, in O_2-saturated 0.1 M $HClO_4$ and at a scan rate of 10 mV s^{-1}. (c) ORR mass activity and (d) ORR polarization curves of the Pt/S-RGO, Pt/L-RGO, and Pt/C catalysts before and after the ADTs, at rotation rate of 1600 rpm, in O_2-saturated 0.1 M

$HClO_4$ and at a scan rate of 10 mV s^{-1}.