

Electronic Supplementary Information

A facile Pt catalyst regeneration process significantly improves the catalytic activity of Pt-organic composites for the O₂ reduction reaction

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Experimental Section

Chemicals.

K₂PtCl₄ (99.9%, Alfa), Cu(NO₃)₂ (99.7%, JT-Baker), NaClO₄ (JT-Baker), H₂SO₄ (Aldrich), and Nafion (NF, 5%) perfluorinated resin in a mixture of lower aliphatic alcohols and water (Aldrich) were used “as is.”

Fabrication of nPt-embedded Nafion (NF(Pt_{nano})) composites.

In our previous study,^{13, 14} an EC' catalytic process, Cu⁺-mediated Pt reduction (CMPR), was successfully used to incorporate monodisperse nPts in the NF as a non-carbon support. In this process, the accumulated Cu⁺ ions resulting from the reduction of Cu²⁺ ions in the cathodic potential sweeping served as a movable mediator in the NF. The Cu⁺ ions were chemically reoxidized to Cu²⁺ ions by PtCl₄⁻ at the interface between the NF and PtCl₄⁻ solution (Scheme 1). During multiple-scan cyclic voltammetry (MSCV),

monodisperse nPts repeatedly formed in the NF and an NF(Pt_{nano}) composite was fabricated by this process.

The electrochemical experiments were accomplished with a CHI 660C potentiostat/galvanostat and a three-electrode electrochemical cell. Ag/AgCl (3.0 M NaCl) and a platinum wire were used as counter electrodes. All potentials in this study were referenced to the reversible hydrogen electrode (RHE), which was calibrated with H₂ oxidation/evolution on a Pt polycrystalline RDE electrode. A GC electrode (BAS, 3.0 mm diameter) or a GC RDE (Pine Instruments, 5.0 mm diameter) was used as a substrate electrode for both NF and NF(Pt_{nano}) composite. The NF(Pt_{nano})-modified GC electrode (NF(Pt_{nano})@GCE) was fabricated by CMPR described in our previous studies.^{13, 14} Briefly, a GC electrode was successively polished with 1.0, 0.3, and 0.05 μm alumina powder cloth (Buchler), followed by sonication in deionized water (specific resistivity = 18.2 MΩ·cm⁻¹) and dried before use. Then, a 5% NF coating solution (4.0–9.0 μL) was spin-coated onto the GC electrode at a spin rate of 3000 rpm. An NF@GC electrode was obtained after approximately 3 min of spinning to allow the solvent to evaporate. The NF(Pt_{nano}) composite was obtained by MSCV between 0.7 V and 0.02 V vs. Ag/AgCl (potential range for Cu²⁺/Cu⁺) in 0.1 M NaClO₄ solution containing 0.1 mM PtCl₄²⁻ and 0.1 mM Cu²⁺. The scan rate was 0.05 V·s⁻¹ at 28 °C. The Pt loading was also controlled by the duration of the sweep cycles in CV. The mass of Pt was directly evaluated from the reduction charge of Cu²⁺ (the production of 1 equiv. Pt was required to consume two equiv. Cu⁺) or confirmed by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The microstructure of NF(Pt_{nano}) composites was observed with a JEOL

JSM-6700F field-emission scanning electron microscope (FE-SEM) and a JEOL JEM-1400 transmission electron microscope (TEM). The TEM samples were prepared by using an NF-deposited Ti grid (NF@Ti) as the working electrode. The NF(Pt_{nano}) composite was formed on a Ti TEM grid by the same procedure on the GC substrate.

Electrodissolution of nPts.

An NF(Pt_{nano})@GCE was used as the working electrode for the electrodisolution of nPts. The NF(Pt_{nano})@GCE was dipped in a 0.5 M NaClO₄ aqueous solution containing 0.5 M HCl under stirred. The anodic MSCV potential was scanned in the anodic direction from 0.6 V to 1.3 V (vs. RHE). The scan rate was 0.01 V·s⁻¹ at 28 °C. The anodic charge used to perform anodic stripping of the nPts from NF(Pt_{nano})@GCEs with a known mass of Pt was evaluated during the anodic MSCV treatment. The oxidation state of the Pt ion was determined in accordance with Faraday's laws of electrolysis.

Electrochemical characterization of oxygen reduction reaction (ORR).

A GC RDE covered with the NF(Pt_{nano}) composite was used as the working electrode for ORR measurements. The as-prepared working electrode was electrochemically cleaned using a cycling potential between 0.0 and 1.0 V (vs. RHE) using 10 cycles in Ar-purged 0.5 M sulfuric acid. The electrochemical surface areas (ECSA) were determined by measuring the areas (charges) under the hydrogen adsorption/desorption peaks of the CVs (scan rate: 0.2 V·s⁻¹) in a 0.5 M sulfuric acid solution. A conversion factor of 0.21 mC·cm⁻² was used to determine the ECSA.¹⁵ ORR experiments were performed in oxygen-saturated 0.1 M HClO₄ aqueous solution.

The solution was purged with oxygen for at least 30 min to ensure oxygen saturation. A three-electrode electrochemical cell was used for the ORR electrochemical experiments. Ag/AgCl and a Pt wire were used as the reference and counter electrodes, respectively; however, all potentials are quoted with respect to a reversible hydrogen electrode (RHE). The scan rate is 0.01 V·s⁻¹. The electrode rotation for RDE voltammetry experiments was provided by a Pine Model AFMSR electrode rotator. The kinetic current for ORR is derived from the Koutecký-Levich equation.¹⁵

$$\frac{1}{j} = \left(\frac{1}{j_k} + \frac{1}{j_D} \right) = \left(\frac{1}{j_k} + \frac{1}{B\omega^{0.5}} \right)$$

where j is the measured current density; j_k and j_D are the kinetic and diffusion current densities, respectively; B is a constant; and ω is the rotation speed. The experimental value of the B factor, 0.091 mA·s^{-0.5}, is close to the calculated value, 0.092 mA·s^{-0.5}, for an ideal 4e⁻ process. Calculation of the B factor ($B = 0.62nFAD_{O_2}^{2/3} \nu^{1/6} C_{O_2}$) was based on published values for the diffusion coefficient of O₂ ($D_{O_2} = 1.93 \times 10^{-5}$ cm²·s⁻¹), kinetic viscosity of the solution ($\nu = 1.009 \times 10^{-2}$ cm²·s⁻¹), concentration of dissolved O₂ in solution ($C_{O_2} = 1.26 \times 10^{-3}$ mol·L⁻¹), Faraday constant (F), and the electrode's geometric area (A). The specific activity was calculated using ECSA. The mass activity was obtained by dividing the kinetic current on 0.90 V by the Pt mass.

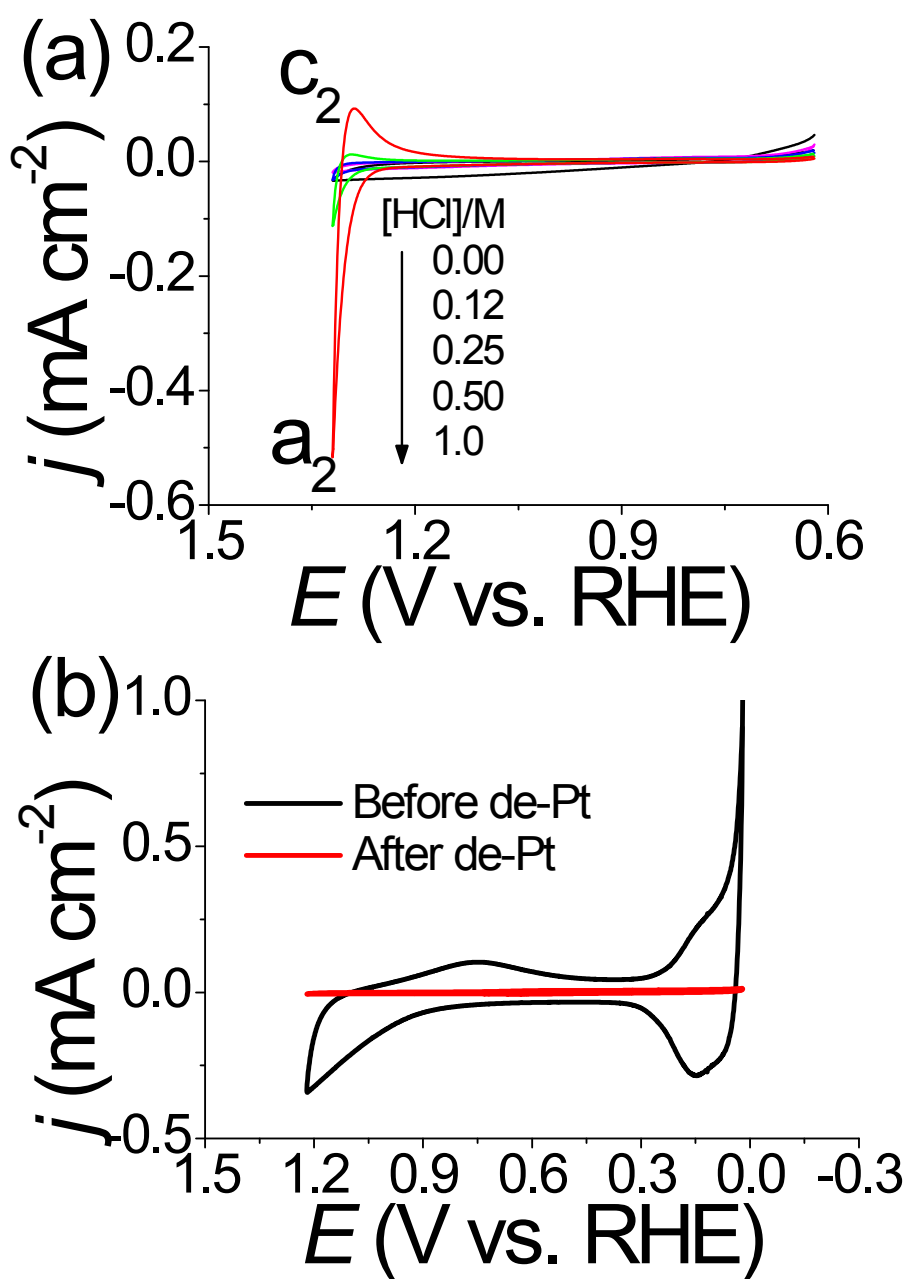


Fig. S1 (a) CVs of bulk Pt were recorded in 0.5 M NaClO₄ aqueous solutions with various concentration of HCl at a scan rate 0.05 V·s⁻¹. (b) CVs of the NF(Pt_{nano})@GCE in 0.5 M H₂SO₄ recorded before and after de-Pt treatment, respectively, at a scan rate 0.2 V·s⁻¹.

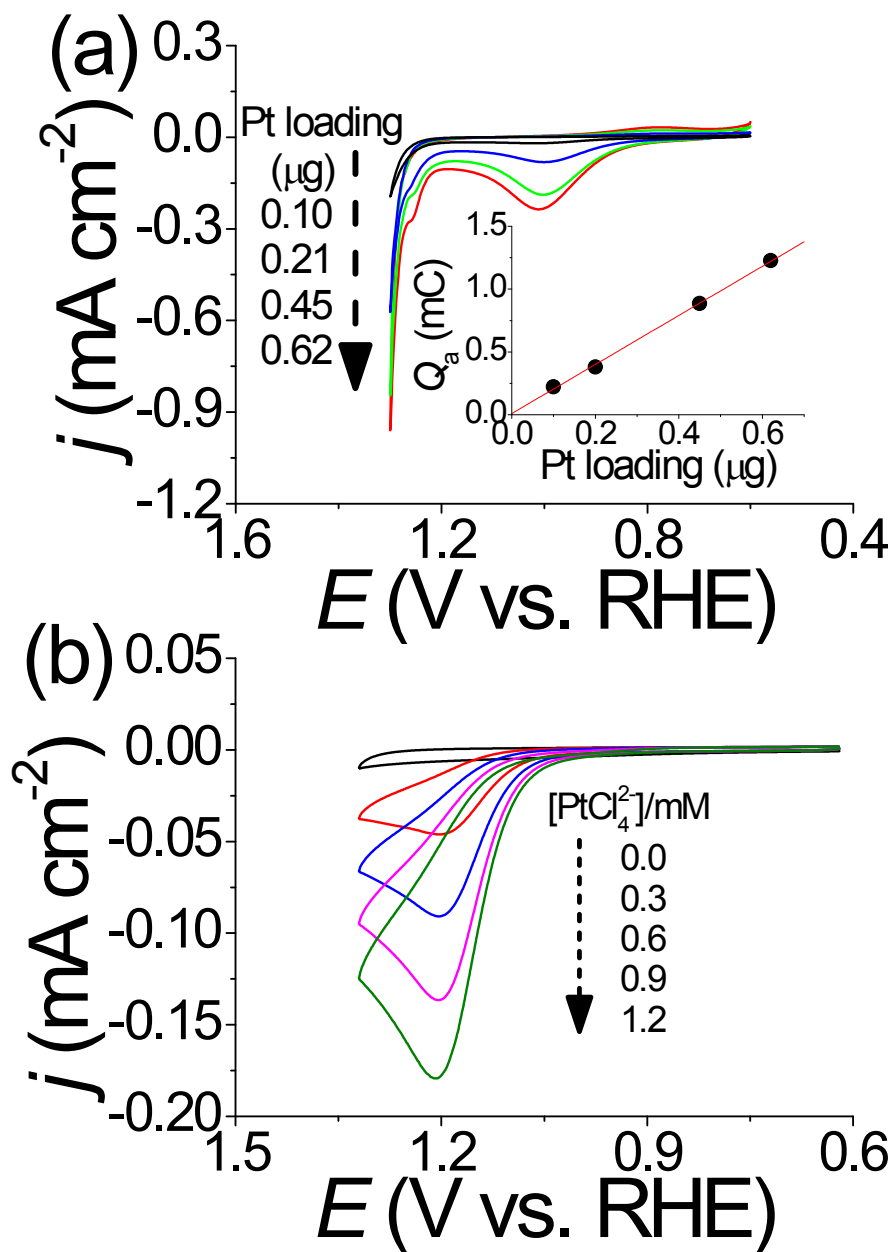


Fig. S2 (a) CVs of NF(Pt_{nano})@GCEs with known mass of Pt (0.10, 0.21, 0.45, and 0.62 μg) were recorded in 0.5 M NaClO₄ solution containing 0.5 M HCl at a scan rate 0.01 V·s⁻¹. The inset is the anodic charge used for anodic stripping of nPts from NF(Pt_{nano})@GCEs vs. the mass of Pt loading. (b) CVs recorded in 0.5 M NaClO₄ solution containing 0.5 M HCl and various concentration of PtCl₄²⁻ at a scan rate 0.01 V·s⁻¹.

Table S1 Results for the anodization of NF(Pt_{nano})@GCE

W_{Pt} (μg)	m_{Pt} (μmol)	$Q_{\text{theory}} (n=1)$ (μC)	Q_{exp} (μC)	n
0.12	0.0006	60.5	241	3.98
0.19	0.0010	96.3	380	3.95
0.41	0.0021	205.1	825	4.02
0.52	0.0027	256.8	1030	4.01

W_{Pt} : the weight of Pt loading in the NF(Pt_{nano})@GCE; m_{Pt} : the number of moles of Pt corresponding to this Pt loading; $Q_{\text{theory}} (n=1)$: the theoretical charge based on W_{Pt} if $n=1$; Q_{exp} : the charge passed during the experiment.

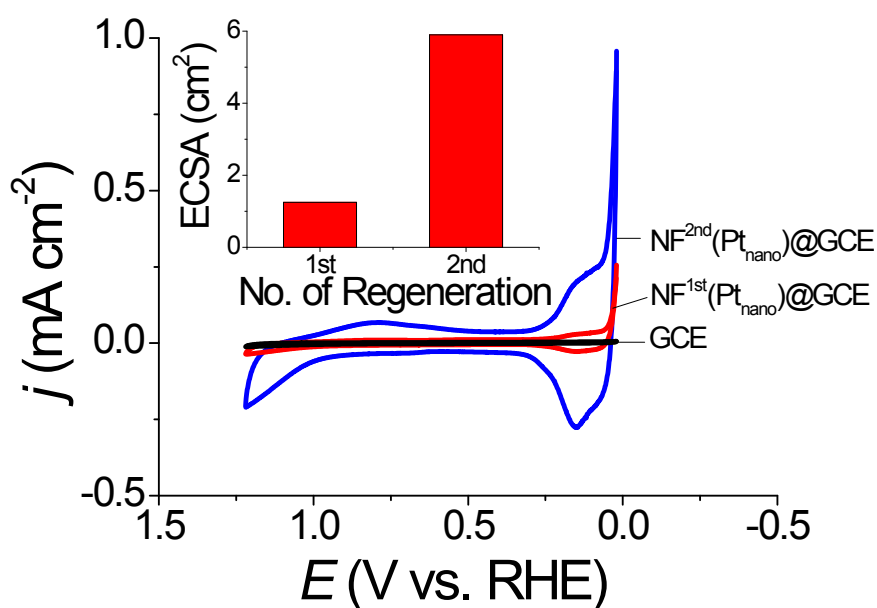


Fig. S3. CVs of NF^{1st}(Pt_{nano})@GCE (Pt loading: 5 $\mu\text{g}\cdot\text{cm}^{-2}$), NF^{2nd}(Pt_{nano})@GCE (Pt loading: 5 $\mu\text{g}\cdot\text{cm}^{-2}$) and GC were recorded in 0.5 M H₂SO₄ at a scan rate 0.2 V·s⁻¹. Inset: ECSA of NF^{1st}(Pt_{nano}) and NF^{2nd}(Pt_{nano}) evaluated from the charge under the voltammetric peaks for hydrogen adsorption or desorption (0.3–0.0 V vs. RHE) using the reported value of 0.21 mC·cm⁻² for a clean Pt surface.

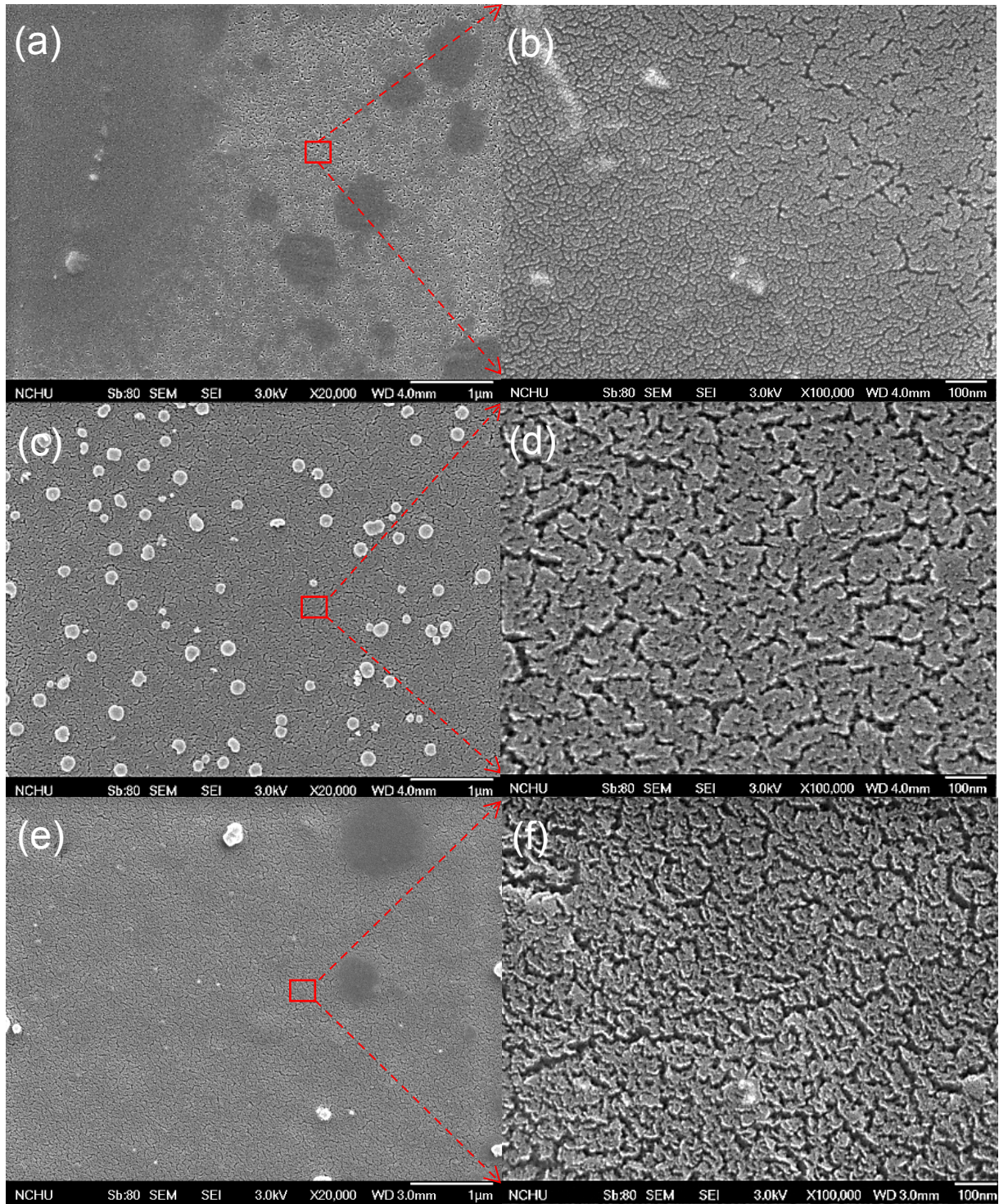


Fig. S4. SEM images of (a) and (b) NF, (c) and (d) NF^{1st}(Pt_{nano}) and (e) and (f) NF^{2nd}(Pt_{nano}); (a), (c), and (e) were taken at lower magnification ($\times 20000$) and (b), (d), and (f) were taken at higher magnification ($\times 100000$).

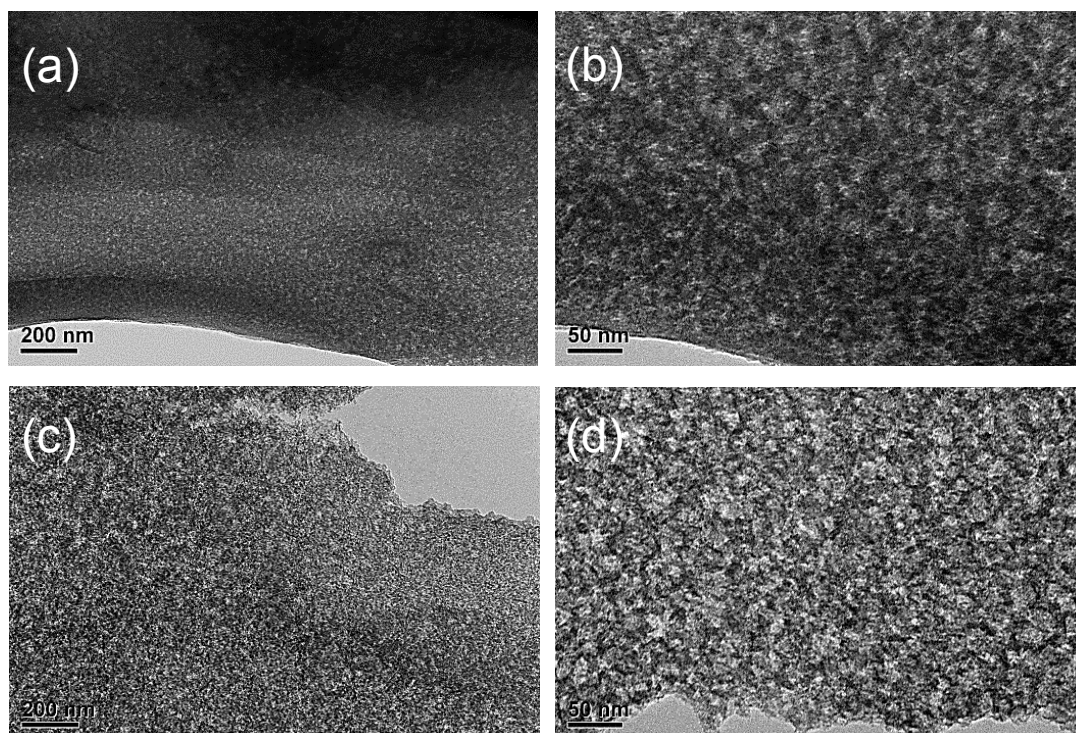


Fig. S5 TEM images of (a) and b) $\text{NF}^{1\text{st}}(\text{Pt}_{\text{nano}})$ and (c) and (d) $\text{NF}^{2\text{nd}}(\text{Pt}_{\text{nano}})$; (a) and (c) were taken at lower magnification ($\times 100000$) and (b) and (d) were taken at higher magnification ($\times 400000$).

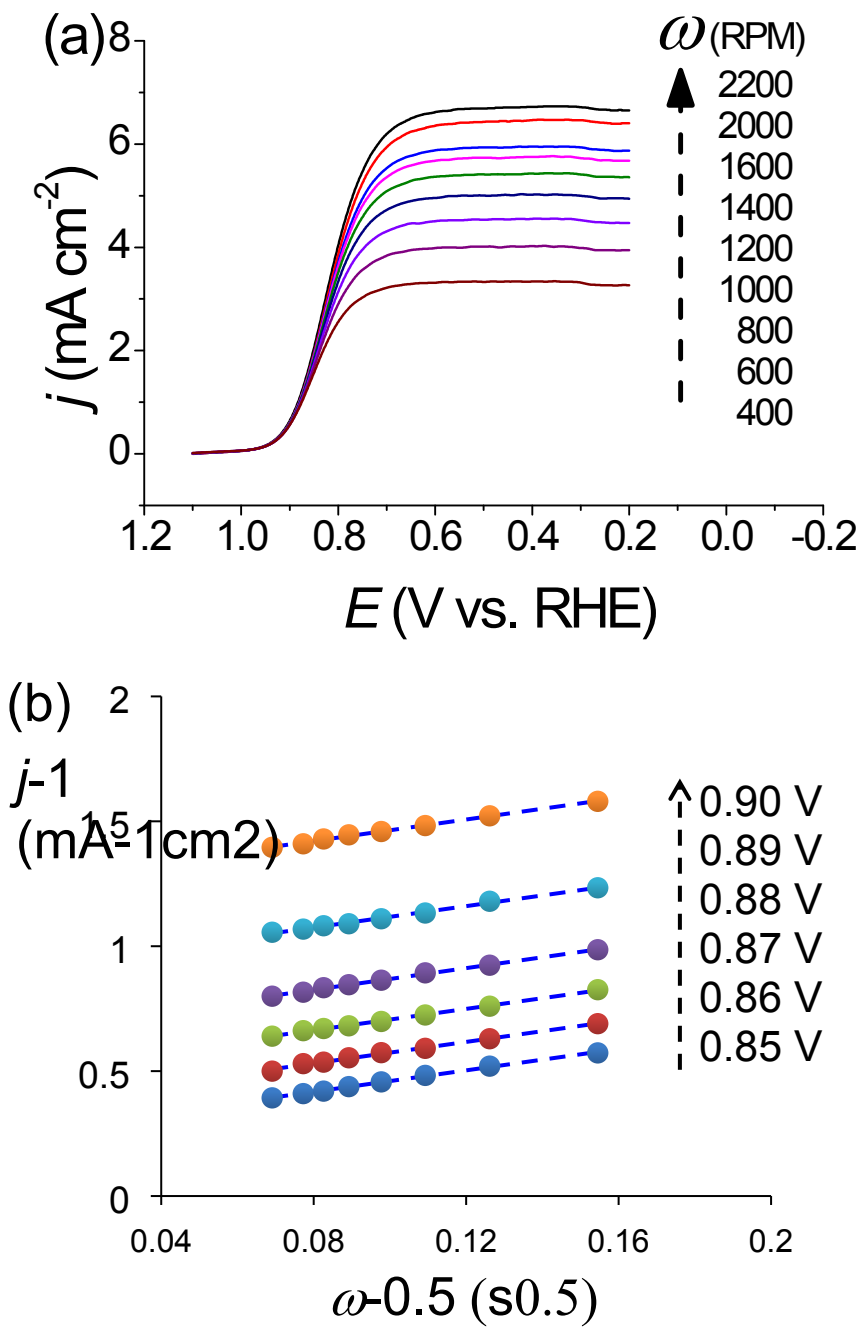


Fig. S6 (a) ORR polarization curves of the NF^{2nd}(Pt_{nano}) composite (Pt loading: 5 $\mu\text{g}\cdot\text{cm}^{-2}$)-modified GC RDE at various rates of rotation at room temperature in O₂-saturated 0.1 M HClO₄ aqueous solution. The scan rate was 0.01 V·s⁻¹. (b) Koutecký-Levich plots at different potentials obtained from the data in (a).