Cu(I)-Mediating Pt Reduction to Form Pt-Nanoparticle-Embedded Nafion Composites and Their Electrocatalytic O_2 Reduction

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Supporting information

Experimental Section

Chemicals: Potassium tetrachloroplatinate 99.9% (Alfa), copper nitrate 99.7% (JT-Baker), sodium nitrate (JT-Baker), sulfuric acid (Aldrich), and Nafion perfluorinated resin (5%) in a mixture of lower aliphatic alcohols and water (Aldrich) were used without purification.

Fabrication of nPts-embedded Nafion (NF(Pt_{nano})) composite: Electrochemical experiments were conducted using a CHI 660C potentiostat/galvanostat. A three-electrode electrochemical cell was used for the electrochemical experiments. Ag/AgCl (3.0 M KCl) and a Pt wire were used as the reference and counter electrodes, respectively. A glassy carbon (GC) electrode (Pine Instruments, 5.0 mm diameter) was used as a substrate electrode for Nafion (NF) membrane or NF(Pt_{nano}) composite. The 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. Next, 6 μl of 5% NF coating solution was spin-coated onto the GC electrode at 3000 rpm. A uniform NF thin film was covered on the GC electrode (NF@GC) by evaporating the solvent at room temperature after about 3 min of spinning. The NF(Pt_{nano}) composite was obtained by multiple-scan CV between 0.7 V and 0.05 V vs. Ag/AgCl (potential range for Cu^{2+}/Cu^{+}) in 0.1 M $NaNO_3$ solution containing 0.1 mM $PtCl_4^{2-}$ and 0.1 mM Cu^{2+}. The scan rate was 50 mV s^{-1} and the temperature was 28°C. The nPt loading was also controlled by the CV sweeping cycle times. The nPt mass was determined directly from the Cu^{2+} reduction charge using Faraday's law of electrolysis. The reduction charge for Cu^{2+}/ Cu^{+} was recorded from the charge under the voltammetric peaks in (0.7– -0.05 V vs. Ag/AgCl). Specifically, 1 eq. nPt must be produced to consume 2 eq. Cu^{+}. The microstructure of nPts in the NF(Pt_{nano}) composite was observed using a JEOL JEM-1400 Transmission Electron Microscope (TEM) and a JEOL JEM-2100F Field Emission Transmission Electron Microscope (FE-TEM). TEM samples were prepared using NF covered Ti TEM grids (NF@Ti) directly as the working electrode. The Ti grid is used as a conducting substrate to support NF film because Ti provides an ideal polarization behavior similar to that on GC substrate in the same potential range. The NF(Pt_{nano}) composite was formed on the Ti TEM grid by the same procedure as on the GC substrate. X-ray photoelectron spectroscopy (XPS) was employed for surface element analysis of the as-prepared NF(Pt_{nano}) composite. XPS data were obtained using an ULVAC-PHI, PHI 5000 VersaProbe/Scanning ESCA Microprobe. Instead of using GC disks, GC plates (from Alfa) were used as the working electrodes for XPS sample preparation. For X-ray diffraction (XRD) measurements (Cu K_{α} radiation), an ITO glass slide (10 × 10 mm) was used as the substrate for NF(Pt_{nano}) composite to avoid interference from the substrate signal. The ITO glass slide was sonicated in acetone and ethanol solutions for 20 min, sequentially rinsed with deionized water (specific resistivity 18.2 $M\Omega\ cm^{-1}$), and dried in an oven before being used as the working electrode. Next, 5% NF was dip-coated onto the ITO glass slide. A uniform NF thin film was deposited on the ITO glass slide (NF@ITO) by evaporation in air at room temperature after about 30 min. The NF(Pt_{nano}) composite was formed on the NF@ITO by the same procedure as on the GC substrate.

Electrochemical measurements: A NF(Pt_{nano}) composite covered GC RDE (Pine Instruments, 5.0 mm diameter) was used as the working electrode for ORR measurement. The as-prepared working electrode was electrochemically cleaned using a cycling potential between 0.0 and 1.0 V (vs. RHE) for 30 times in an 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 cyclic voltammograms (scan rate, 0.2 V s^{-1}) in a 0.5 M sulfuric acid solution. A conversion factor of 210 $\mu C\ cm^{-2}$ was used to determine the ECSA.[15] Oxygen reduction reaction (ORR) experiments were performed in oxygen-saturated 0.1M $HClO_4$ aqueous solution. The solution was purged for at least 30 min to ensure oxygen saturation. A three-electrode electrochemical cell was used for the ORR electrochemical experiments. Ag/AgCl (3.0 M KCl) 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 rates for ORR in CV and RDE measurements were 50 mV/s and 10 mV/s, respectively. The necessary 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.[42]

$$\frac{1}{j} = \left(\frac{1}{j_{\mathrm{k}}} + \frac{1}{j_{\mathrm{D}}}\right) = \left(\frac{1}{j_{\mathrm{k}}} + \frac{1}{B\omega^{0.5}}\right)$$

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 O_2 ($D_{O_2} = 1.93 \times 10^{-5}$ $cm^2\ s^{-1}$), kinetic viscosity of the solution ν ($\nu = 1.009 \times 10^{-2}$ $cm^2\ s^{-1}$), concentration of dissolved O_2 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 nPt mass.

Figure s1.

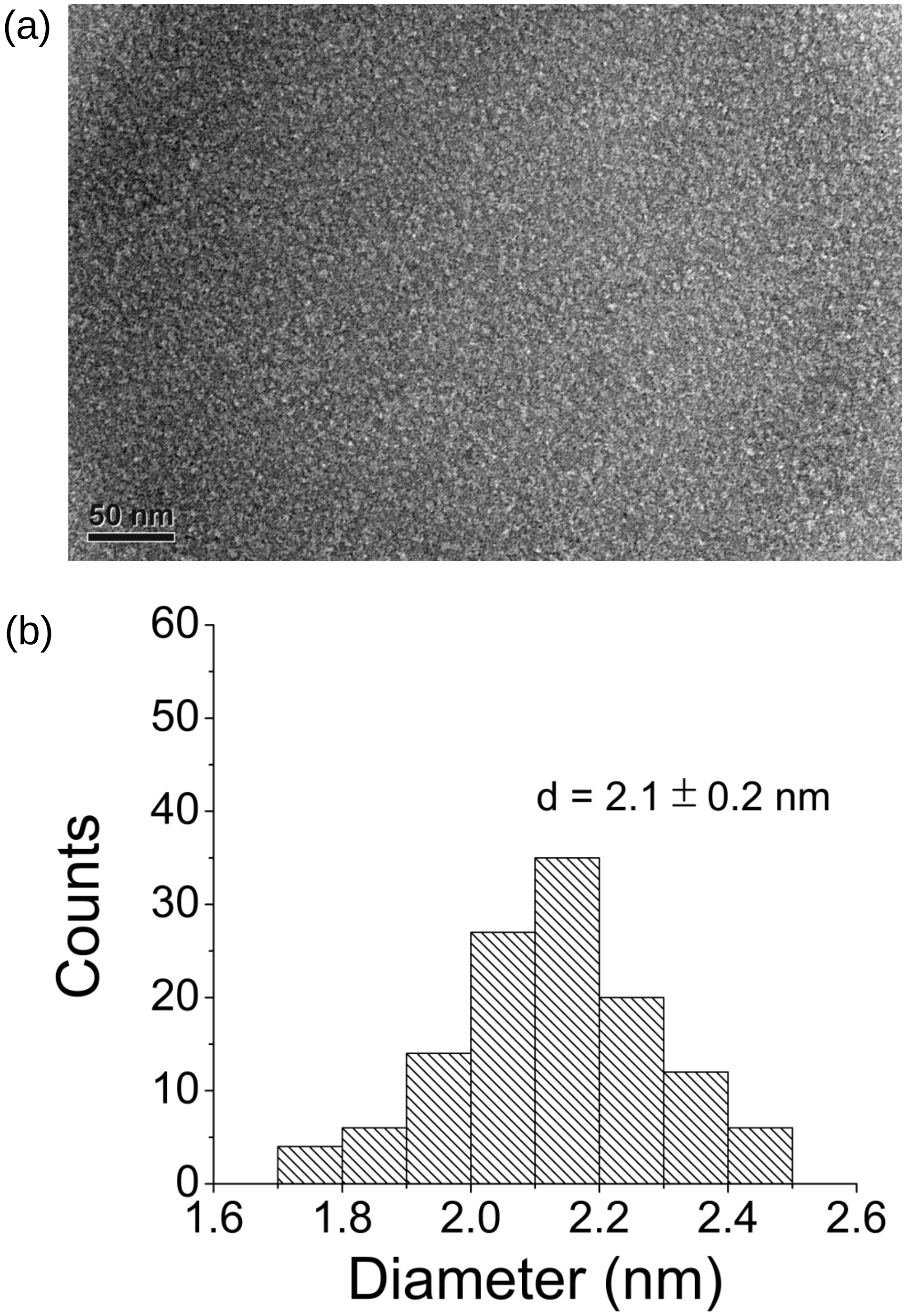

Figure s1. (a) TEM image and particle-size distribution of nPts in the NF(Pt_{nano}) composite covered Ti grid. (b) The prticle-size distribution is based on 120 randomly selected particles in a).

Figure s2.

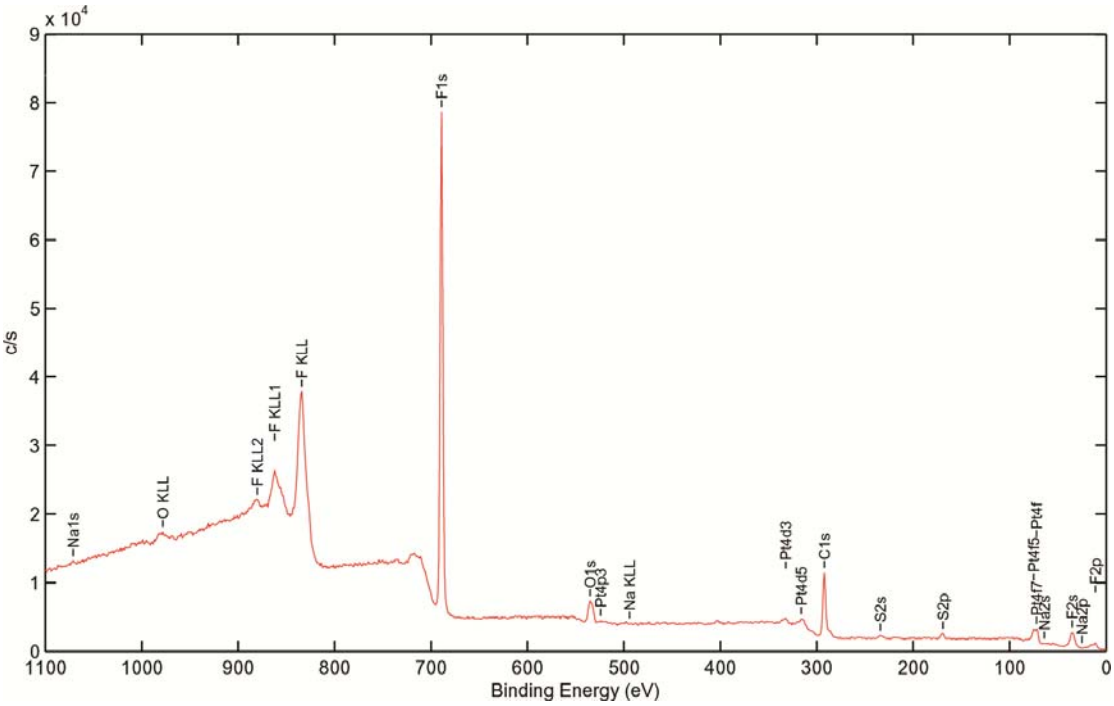

Figure s2. A XPS spectrrum of the NF(Pt_{nano}) composite.

Figure s3.

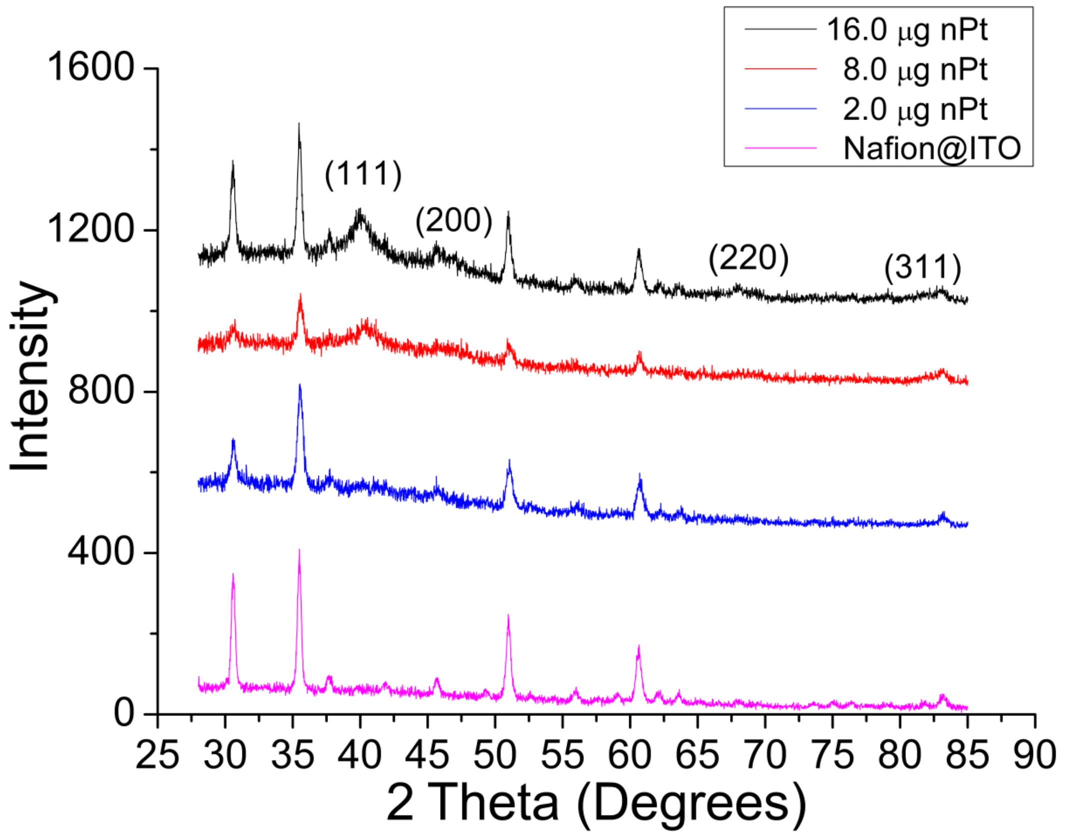

Figure s3. XRD patterns (Cu K_{α}) of a series of NF(Pt_{nano}) composites were obtained on the Nafion covered ITO (Indium Tin Oxide) slide (10 mm × 10 mm) and the bare Nafion covered ITO substrate. The reflection patterns were assigned in accordance with JCPDS card no. 882343 for Pt.

Figure s4.

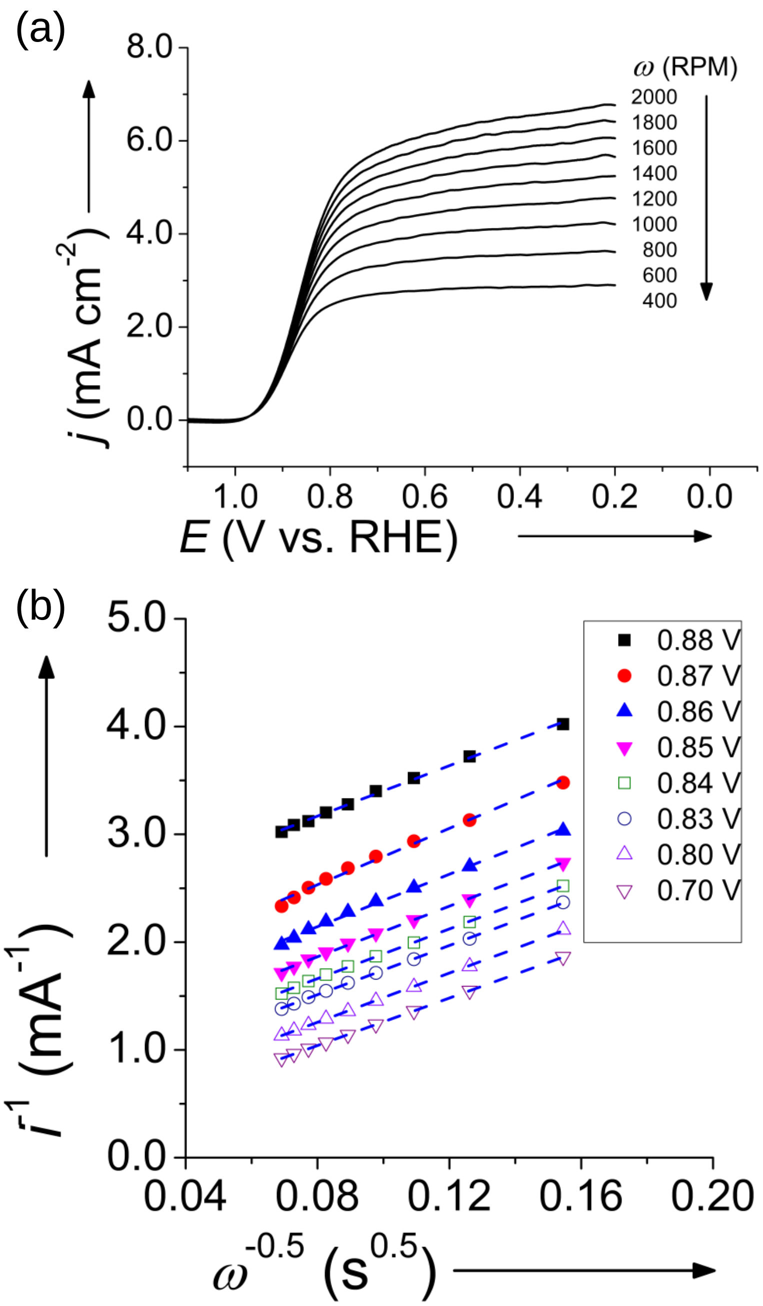

Figure s4. (a) ORR polarization curves of the NF(Pt_{nano}) composite (nPt loading is 40.0 μg cm^{-2}) modified GC RDE at various rates of rotation recorded at room temperature in O_2-saturated 0.1 M $HClO_4$ aqueous solution. The scan rate was 10 mV/s. (b) Koutecký-Levich plots at different potentials obtained from the data in (a).

Figure s5.

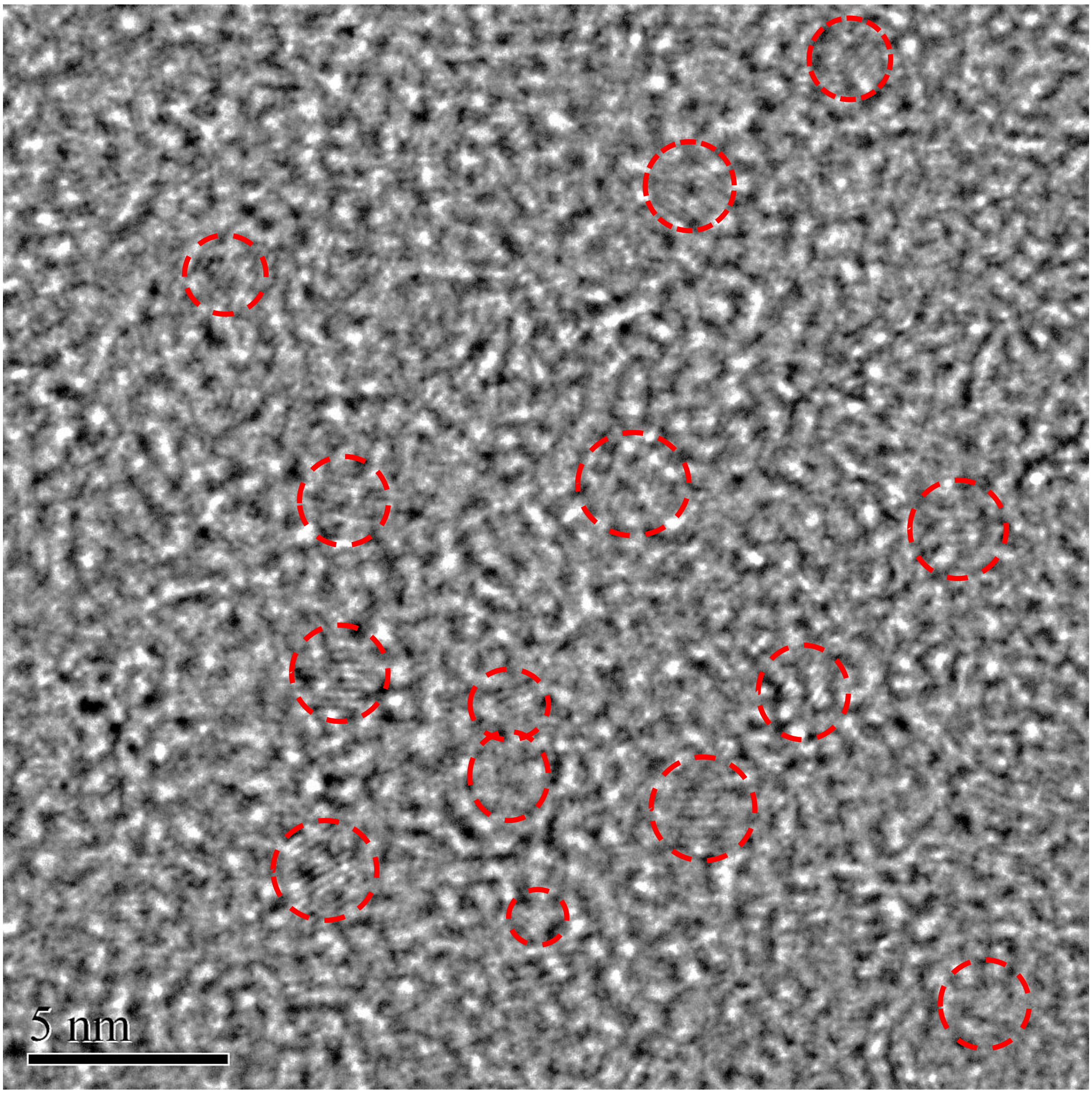

Figure s5. High-resolution TEM of the nPts in the NF(Pt$_{nano}$) composite covered Ti grid. The nPts are marked by red dash circles.