In-situ solution plasma synthesis of mesoporous nanocarbon-supported bimetallic nanoparticles

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Methodology and experimental conditions

We describe the methodology and experimental conditions in detail as follow, and it added in ESI.

Solution plasma processing
Experiments were carried out in the room temperature and atmospheric pressure conditions. Metal wires (Au, Pt) with diameter of 1.0 mm(W, Co, 99.95% Nilaco, Japan) and benzene (C_6H_6, 99.5% Kanto Chemical, Japan) were applied, respectively, as the precursors of Au, Pt and carbon nanoparticles. To concentrate energy, each electrode was insulated by ceramic tubes; protruding length was 1.5 mm from the ceramic tube tips and tubes were inserted into a silicone plug. One pairs of metal electrodes (Au, Pt) was placed in a glass vessel (100 ml beaker, with a diameter of 5 cm and height of 7 cm); the distance between the tips of the electrodes was set at 0.5 mm. The electrodes were discharged in benzene using a bipolar–DC pulse power supply (Kurita, Japan); the voltage, pulse frequency, and pulse width were controlled at 1.6 kV, 25 kHz, and 0.5μs, respectively
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Drying of sample
To get carbon powder, discharged solution was filtered by glass microfiber filter (1.0 μm) and dried in oven at 80°C for 1hours.

Heat treatment
This process was performed in a tube furnace with a 20 minute dwell time, under a flowing Ar atmosphere, with a heat treatment temperature (HTTs) of 700 °C(heating rate : 25°C/min, cooling rate : 7°C/min.)

Characterization
Transmission electron microscopy (TEM, JEOL, JEM2500SE at 200 kV) observations were conducted to study the microstructure, shape and size of the synthesized smaple. X-ray diffraction patterns (XRD, Rigaku Smart lab) were obtained using Cu Kα (λ = 1.54 nm) as a target over a scan range of 30–50° with 0.02° step size and 2° min^{-1} scan speed. The specific surface area, total pore volume, and pore diameter of all of the samples were calculated by N_2 adsorption–desorption isotherms using the Brunauer–Emmett–Teller (BET) method (Belsorp-mini II, Belsorp). All samples were degassed at 200 °C for 2 h prior to measurement of the BET.

Electrode preparation and electrochemical characterization
In order to evaluate the electrochemical properties of bimetallic NPs/C, three electrode cells with a potentiostat (Hokuto Denko Inc. HZ5000, Japan) were applied. The three-electrode cell consisted of a glassy carbon (GC) disk (3 mm in diameter) working electrode, Ag/AgCl (saturated KCl) reference electrode, and a counter electrode made of platinum wire. The

samples were prepared by ultrasonicating a mixture of 5 mg of sample powder, 0.5 ml of ethanol, and 50 ml of Nafion solution (Aldrich, 5 wt% Nafion) until a homogeneous suspension was formed. A droplet (10 μl) of the obtained suspension was placed on the glassy carbon and dried at room temperature prior to the measurement. The cyclic voltammetry (CV) method was conducted in 1 M H_2SO_4 electrolyte and N_2 gas was purged in the solution at a 50 mVs–1 scan rate from –0.2 V to 1.4 V (V vs. Ag/AgCl).

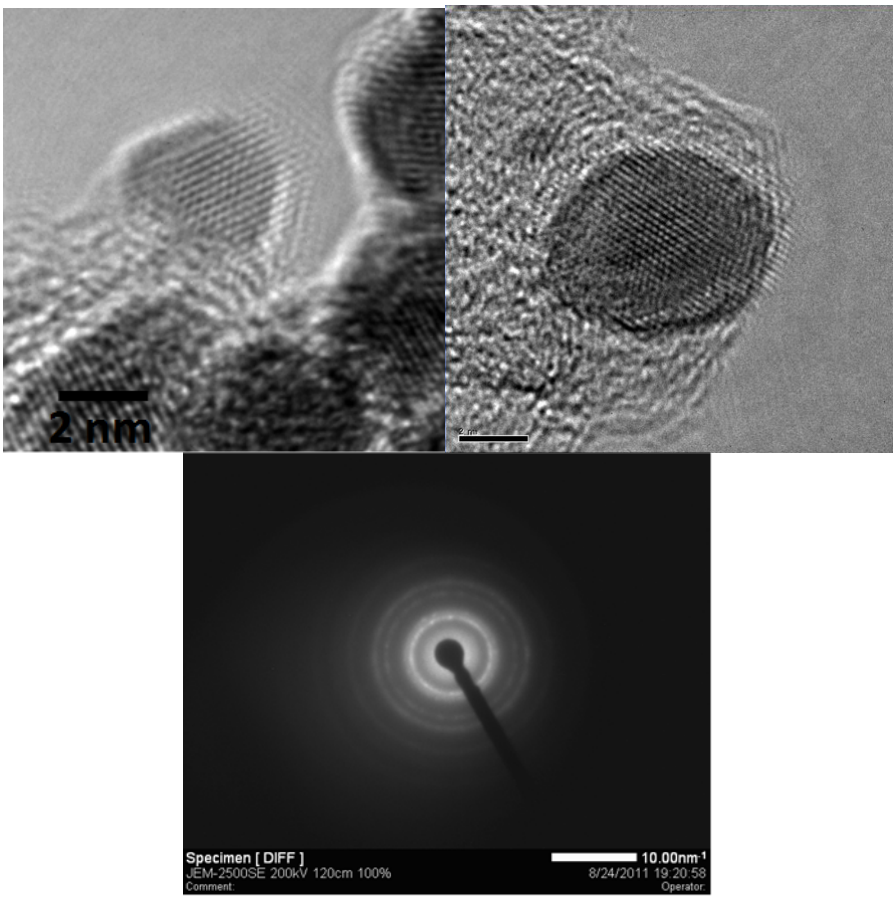

Fig. S1 (up) a selected area diffraction pattern (SAED)
(down) HRTEM image of AuPt bimetallic NPs/C.

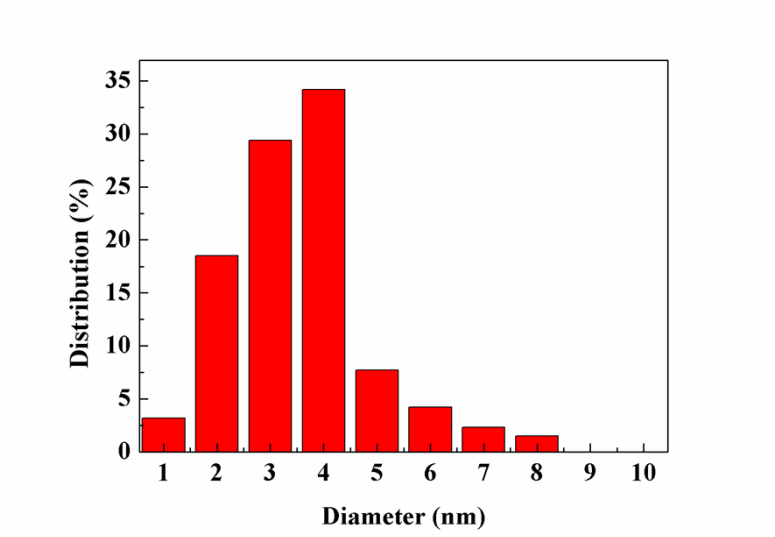

Fig. S2 size distribution of AuPt bimetallic NPs;

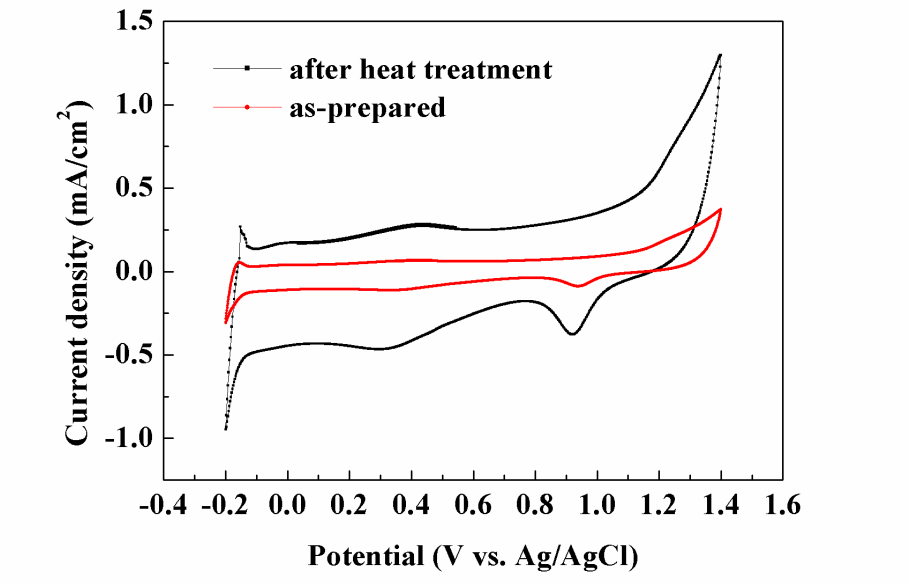

Fig. S3 Cyclic voltammetry plots for AuPt bimetallic NPs/C ; The as-prepared samples show little electrocatalytic area than the annealed sample because carbon's resistivity is larger than that of the annealed sample due to its low crystallinity. However, they show similar ORR, HER tendency with heat treated samples. On the other hands, It should be noted that AuPt nano particles possibly be incorporated or embedded in the carbon particles. However as shown in CV graphs, AuPt bimetallic NPs show the large electorcatalytic area and thus it is assumed that alomost NPs supported on carbon blacks.

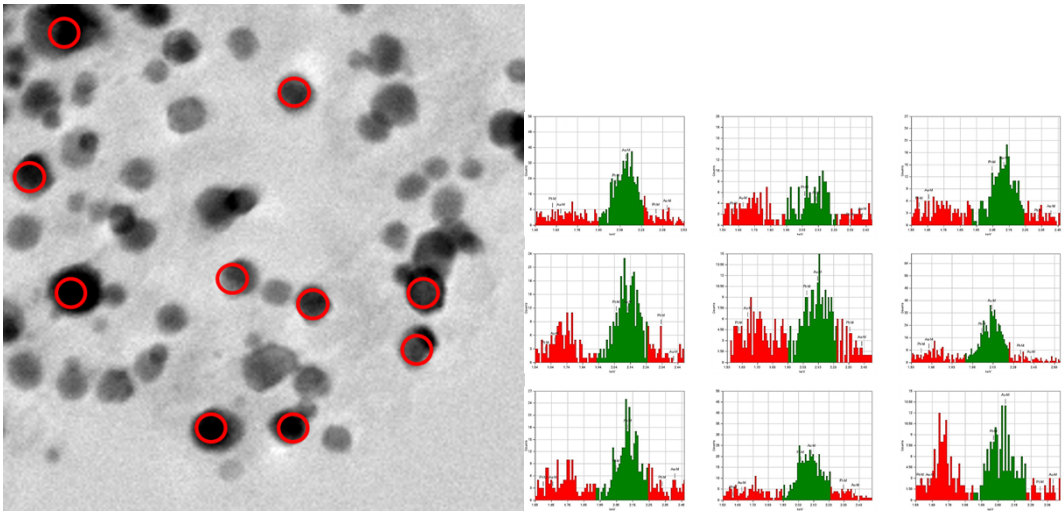

Fig. S4 EDS spectrums of AuPt NPs

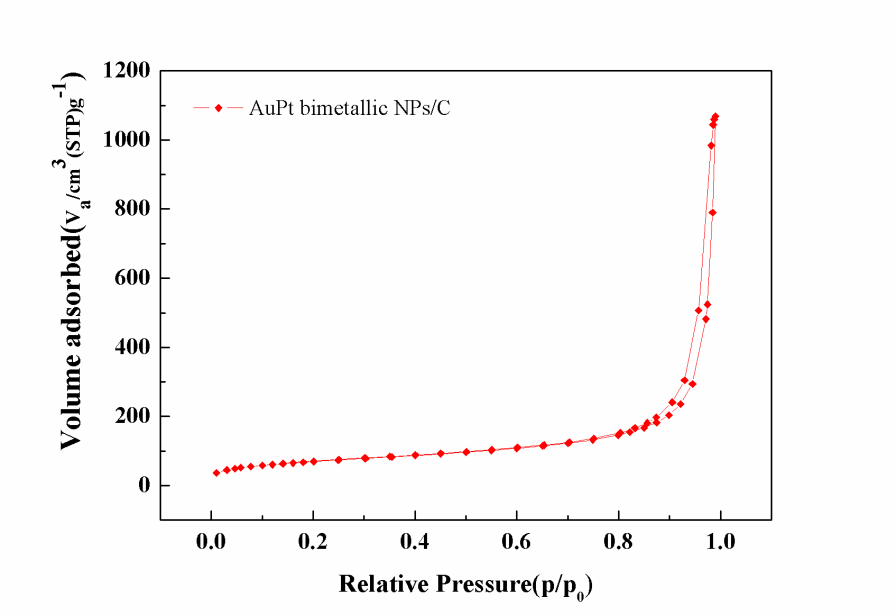

Fig. S5 Nitrogen adsorption–desorption isotherms for AuPt bimetallic NPs/C.

Table S1 Structural parameters of AuPt bimetallic NPs/C.

Sample	Surface area (m^2g^{-1})	Pore volume (m^3g^{-1})	Mean pore diameter (nm)
AuPt bimetallic NPs/C	331	1.42	14.6