Element-saving preparation of an efficient electrode catalyst based on self-assembly of Pt colloid nanoparticles onto an ITO electrode

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Supporting Information

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1. Experimental details

Materials

Hydrogen hexachloroplatinate(IV) hexahydrate (H_2PtCl_6•$6H_2O$) and trisodium citrate dihydrate ($Na_3C_6H_5O_7$•$2H_2O$) were purchased from Kanto Kagaku Co., Ltd. The purest grade of all the chemicals were used as received. ITO-coated glass (10 Ω/□) was purchased from Asahi Glass Co., Ltd. Deionized water was used for all the experiments.

Preparations

Pt colloid solution

A Pt colloid solution was prepared according to the procedure described by Brugger et al. (*J. Am. Chem. Soc*., 1981, **103**, 2923). H_2PtCl_6•$6H_2O$ (7.8 mg, 15 μmol) was added to an aqueous solution (49 mL). A 0.84 mol L^{-1} $Na_3C_6H_5O_7$•$2H_2O$ (1 mL) aqueous solution was added in the solution immediately after refluxing in an oil bath. The mixed solution was additionally refluxed for 45 min to yield a dark brown solution. The solution (0.3 mmol L^{-1}) of Pt colloid was cooled in an ice bath and then stocked in a glass-stoppered flask at 5°C. The stocked solution is stable for several months.

Pt modified electrodes

The Pt colloid solution was adjusted to pH = 4.0 with a dilute HNO_3 solution. An ITO electrode (1.0 cm^2) was immersed in the solution (typically, 0.3 mmol L^{-1}, pH = 4.0) for 3 h to yield a Pt colloid-assembled (PCA) electrode. 53 μL of 0.1 mmol L^{-1} H_2PtCl_6 solution in ethanol was cast on an ITO electrode (1.0 cm^2) and air-dried, and then sintered at 400˚C to yield a Pt thermal-deposited (PTD) electrode.

Measurements

Quartz Crystal Microbalance (QCM) measurement was conducted in a well-type QCM cell equipped with an ITO-sputtered quartz crystal (surface area, 0.196 cm^2) using a quartz crystal analyzer (SEIKO EG&G, QCA922-10). The coverage of self-assembled Pt on the electrode was measured by analyzing Pt dissolved from the electrode with concentrated HCl using an inductively coupled plasma (ICP) mass spectrometer (Yokogawa, HP4500). Scanning electron microscopic (SEM) measurement was carried out using a scanning electron microscope

(JEOL JSM-6510LV). Atomic force microscopic (AFM) data were recorded using an AFM apparatus (SII SPI3800N) in a dynamic force mode. Transmission electron microscopic (TEM) measurement was carried out using a transmission electron microscope (Hitachi Science Systems H-7600). Small angle X-ray scattering (SAXS) data were taken using a rotating anode X-ray generator (Rigaku RU-200). SAXS data were recorded using a linear (one-dimensional) position sensitive proportional counter (Rigaku PSPC). Cyclic voltammograms (CVs) were measured in a 0.1 mol L^{-1} KNO_3 aqueous solution (pH = 1.2) at 20 mV s^{-1} in a conventional single-compartment electrochemical cell equipped with an ITO or a modified ITO electrode as a working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum wire as a counter electrode. Electrochemical proton reduction was conducted in a 0.1 mol L^{-1} KNO_3 aqueous solution (pH = 1.0) under the potentiostatic conditions at -0.8 V vs. Ag/AgCl using a gas-tight single-compartment electrochemical cell. Gas evolved in the electrochemical reaction was analyzed on a gas chromatograph (Shimadzu, GC-8A) equipped with a molecular sieve 5Å column using argon carrier gas (flow rate is 40 mL min^{-1}) at 50°C. All the electrochemical experiments were implemented under argon atmosphere at 25°C using an electrochemical analyzer (Hokuto Denko, HZ-3000).

2. TEM image of Pt colloid.

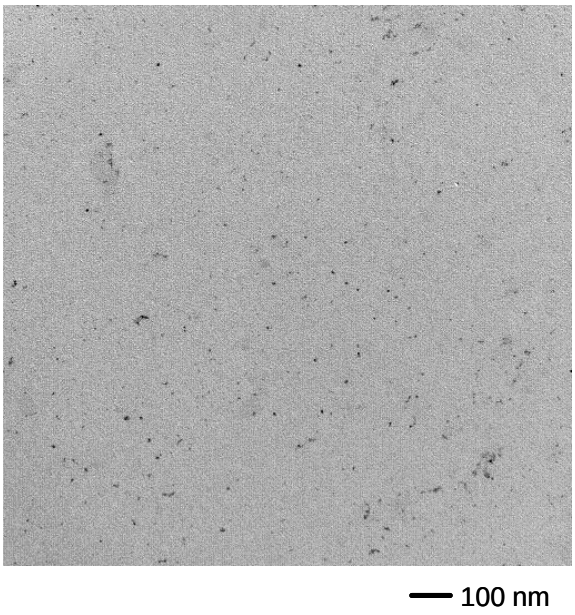
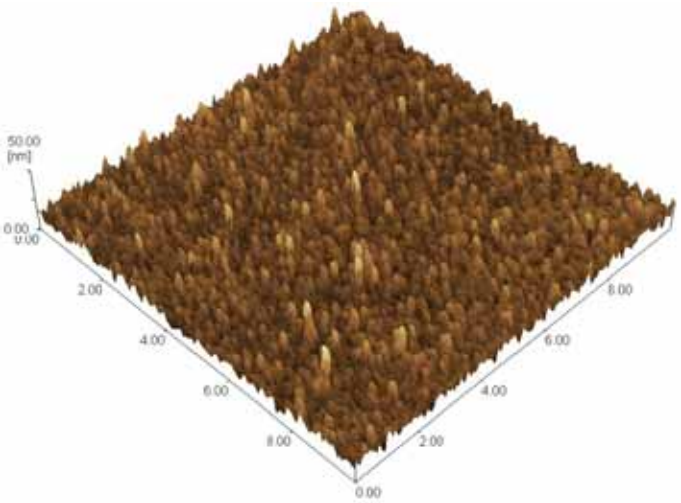


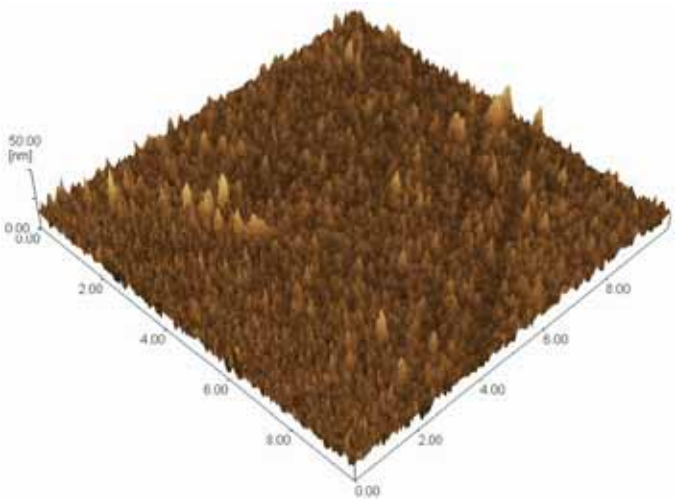
Figure S1 TEM image of Pt colloid particles used. The average diameter was ca. 5 nm.

3. AFM images of the PCA and PTD electrode surfaces.

(a) Bare ITO electrode surface



(b) PCA electrode surface



(c) PTD electrode surface

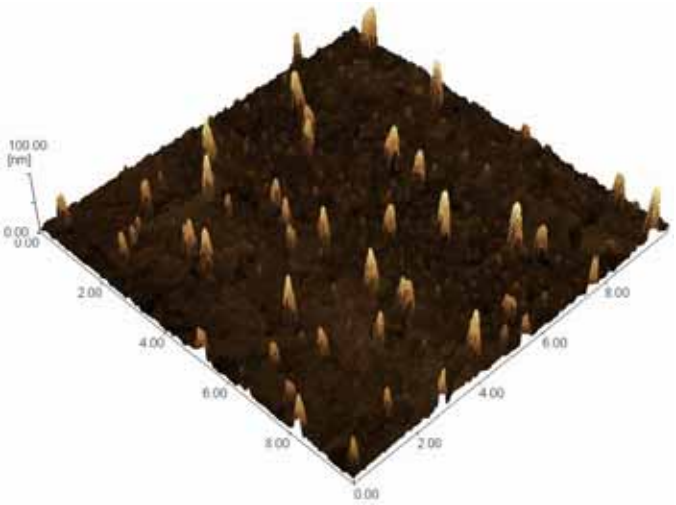
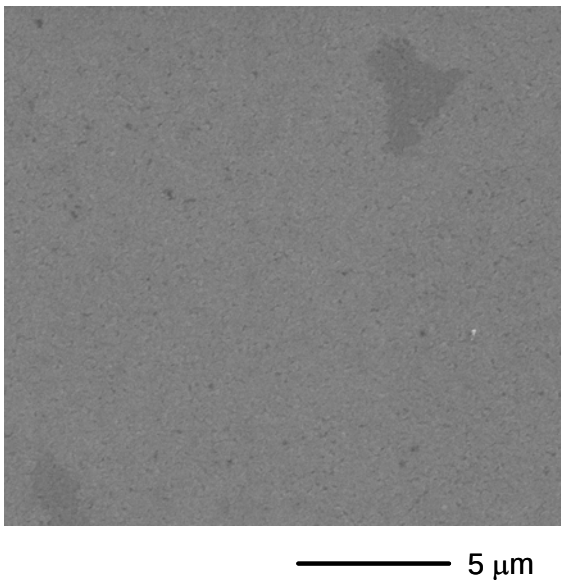


Figure S2 AFM images of (a) bare ITO, (b) the Pt colloid-assembled (PCA) and (c) Pt thermal-deposited (PTD) electrode surfaces.

4. SEM images of the PCA and PTD electrode surfaces.

(a) bare-ITO electrode surface



(b) PCA electrode surface

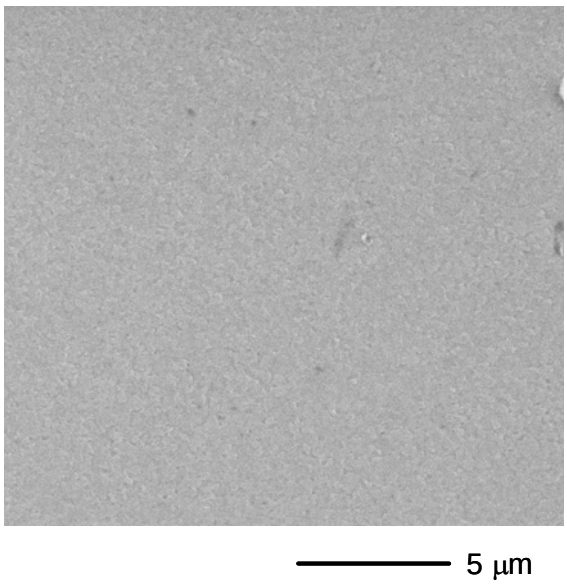


Figure S3 SEM images of (a) bare ITO and (b) the PCA electrode surfaces.

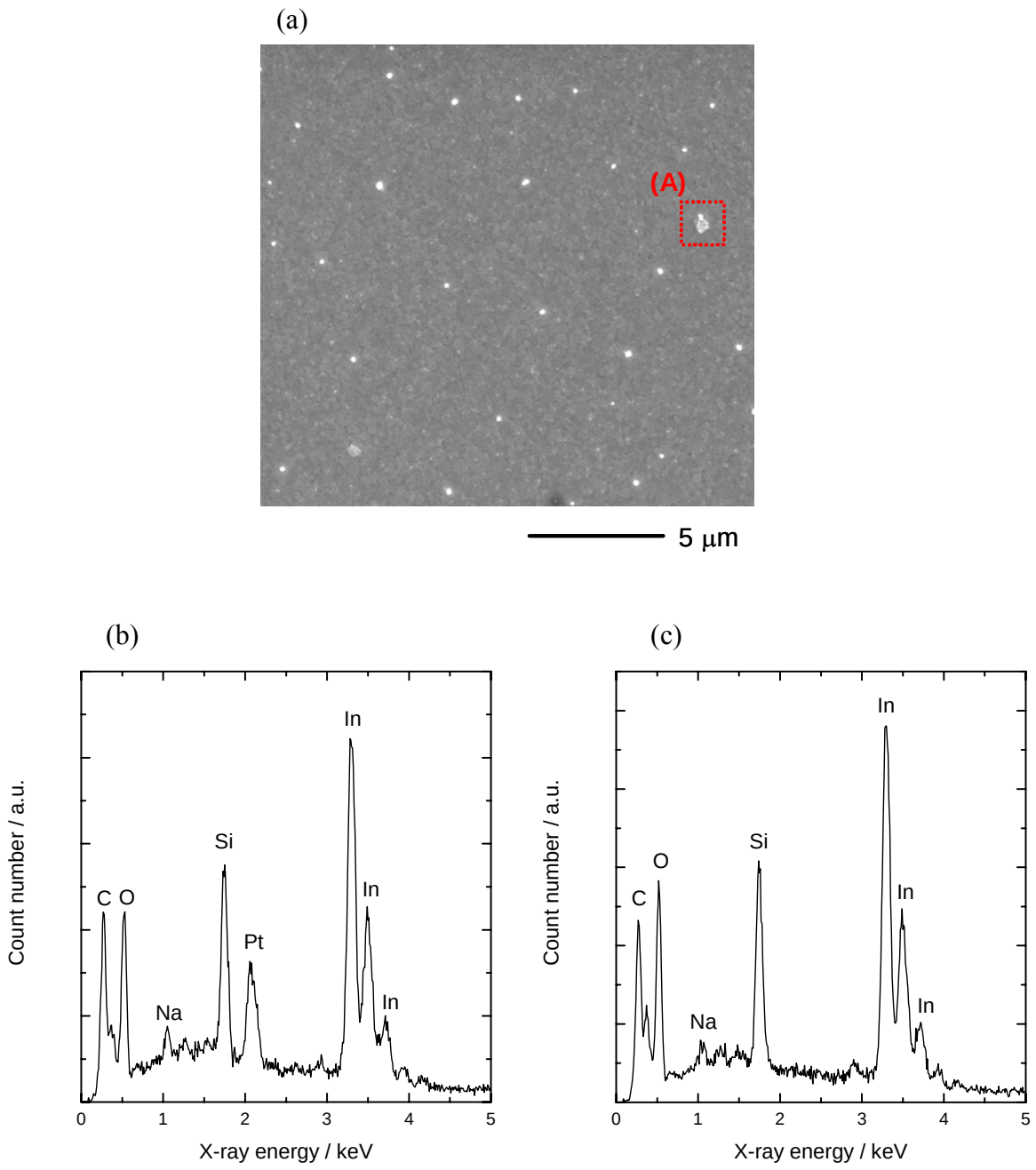


Figure S4 (a) SEM image of PTD electrode surfaces. (b) EDS spectrum at the part (A) containing a white cluster on the PTD electrode. (c) EDS spectrum at the black bulk part on the PTD electrode. The peak at 2.048 keV assigned to Pt on the EDS spectrum corroborates that the white cluster on the SEM image (a) shows Pt particles thermally deposited on the PTD surface.