

Electronic Supplementary Information

Templated Bipolar Electrolysis for Fabrication of Robust Co and Pt
Nanorods

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Experimental

Materials

Cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), hydroquinone (HQ), hexachloroplatinic(IV) acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), and anhydrous acetonitrile (MeCN) were purchased from Wako. Platinum(II) acetylacetonate ($\text{Pt}(\text{acac})_2$) was purchased from Aldrich. Tetrabutylammonium perchlorate was purchased from Tokyo Chemical Industry. All reagents and dry acetonitrile were used without further purification. All aqueous solutions were prepared with deionized water. Electrolytic solutions were deaerated by an intensive Ar bubbling just before use. Anodic aluminum oxide (AAO) membrane (200 nm pore size, 60 μm thickness, 13 mm diameter, Anodisc 13) was purchased from Whatman. Indium-tin-oxide (ITO) glass plates (10 Ω/\square) were purchased from Kinoene Optical Co. Ltd.

Instruments

Direct current (DC) power was supplied to the feeder electrodes using an EC1000SA AC/DC power source (NF Corporation). Optical microscope observations were conducted with an Olympus SZX10, Laser microscope observations were conducted with a Keyence VK-X1000, and scanning electron microscopy (SEM) observation was performed using a Shimadzu SS-550. Cyclic voltammetry (CV) measurements were carried out using an ALS 6005C Electrochemical Analyzer.

Cell configuration

The glass cell equipped with Pt feeder electrodes (20 mm \times 20 mm, distance: 60 mm) was filled with an electrolytic solution. An AAO membrane (200 nm pore size, 60 μm thickness, 13 mm diameter) coated on one side with Au was embedded on an ITO (20 mm \times 20 mm) with epoxy resin, which was also connected to another ITO (20 mm \times 20 mm) with a stainless-steel wire (length: 0.5 or 2 cm). This complex material was placed between the feeder electrodes to be a BPE.

Estimation of ΔV_{BPE}

The minimum applied voltage required to induce BPE (ΔV_{min}) was estimated from the difference between the oxidation and reduction potentials of the corresponding species, E_{ox} and E_{red} , (Eq. 1), as previously reported.¹

$$\Delta V_{min} = |E_{ox} - E_{red}| \quad (1)$$

In this system, the oxidation of HQ and the reduction of Co^{2+} , Pt^{2+} , or $[PtCl_6]^{2-}$ were assumed to occur simultaneously on the BPE. By using the onset potentials of these half reactions (Fig. S1–S3), ΔV_{min} was estimated using Eq. 2, Eq. 3, or Eq. 4

$$\Delta V_{min} = |E_{ox} - E_{red}| = |1.71 \text{ V} - (-1.41 \text{ V})| = 3.12 \text{ V} \quad (2)$$

$$\Delta V_{min} = |E_{ox} - E_{red}| = |1.71 \text{ V} - (-1.19 \text{ V})| = 2.90 \text{ V} \quad (3)$$

$$\Delta V_{min} = |E_{ox} - E_{red}| = |1.71 \text{ V} - (-0.08 \text{ V})| = 1.79 \text{ V} \quad (4)$$

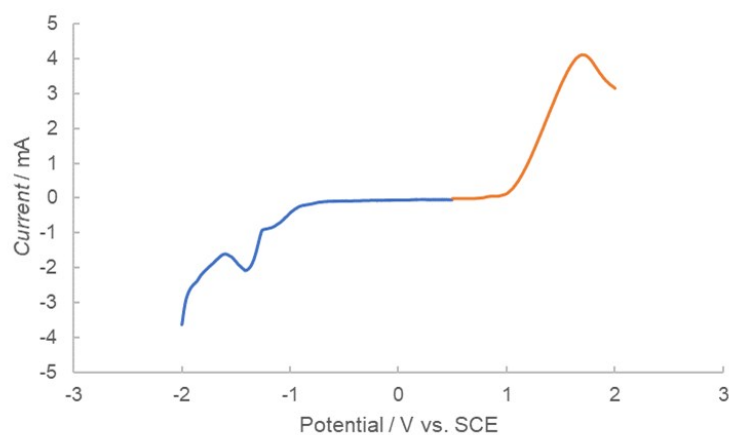


Fig. S1 Linear sweep voltammograms of $CoCl_2$ (10 mM) and HQ (10 mM) measured independently in 0.1 M $Bu_4NClO_4/MeCN$ using an Au working electrode (10 mm \times 10 mm) for 0.5–2 V and a ITO working electrode (10 mm \times 10 mm) for 0.5–2 V, respectively, at a scan rate of 100 mV/s.

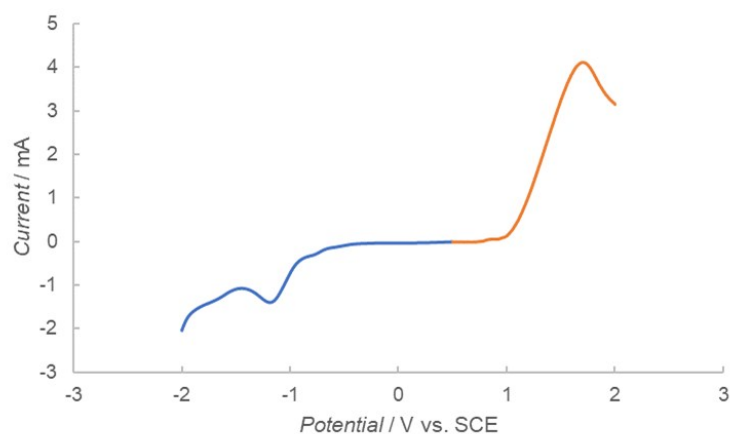


Fig. S2 Linear sweep voltammograms of Pt(acac)₂ (10 mM) and HQ (10 mM) measured independently in 0.1 M Bu₄NClO₄/MeCN using an Au working electrode (10 mm × 10 mm) for 0.5–2 V and a ITO working electrode (10 mm × 10 mm) for 0.5–2 V, respectively, at a scan rate of 100 mV/s.

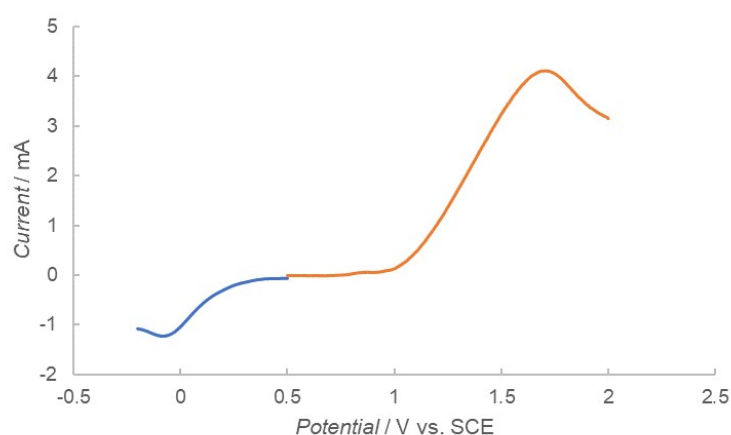


Fig. S3 Linear sweep voltammograms of H₂PtCl₆ (10 mM) and HQ (10 mM) measured independently in 0.1 M Bu₄NClO₄/MeCN using an Au working electrode (10 mm × 10 mm) for 0.5–2 V and a ITO working electrode (10 mm × 10 mm) for 0.5–2 V, respectively, at a scan rate of 100 mV/s.

Template-based Constant Potential Electrolysis in a Conventional Method

50 mM of metal salt (CoCl₂ or Pt(acac)₂) was dissolved in 0.1 M TBAP/MeCN. AAO membrane (200 nm pore size, 60 μm thickness, 13 mm diameter) coated on one side with Au was embedded on an ITO (20 mm × 20 mm), which was utilized as a cathode. After the template was immersed and impregnated with the electrolyte for 30 min, the constant potential electrolysis (−1.8 V vs. SCE) was

performed for the electrodeposition of Co and Pt by applying 2.2 C and 1.0 C, respectively, with a Pt plate anode. After the electrolysis, the ITO with a AAO membrane was removed completely by immersing it in 1 M KOH aq for 12 h. The resultant sample was carefully washed with water and MeCN, and dried.

Estimation of Cell Factors and ΔV_{BPE}

In order to estimate a cell factor, i.e., the electric field transmission efficiency θ , a ratio of electric field inside the cell (ε_{eff}) and applied electric field between driving electrodes (ε) is defined as follows.^{1,2}

$$\theta = \frac{\varepsilon_{\text{eff}}}{\varepsilon} \quad (5)$$

It follows that

$$\theta = \frac{U_m d_E}{d_m E} \quad (6)$$

and

$$U_m = \theta \frac{d_m E}{d_E} \quad (7)$$

where U_m is the potential difference measured between two microelectrodes with distance of d_m , E is the applied voltage between the driving electrodes set with distance of d_E (Fig. S4). Based on Eq. 7, a value of ε can be estimated from slope of plots of U_m as a function of Ed_m/d_E ; thus, a potential applied between each bipolar electrode (ΔV_{BPE}) can be estimated as follows:

$$\Delta V_{BPE} = \theta \frac{d_{BPE} E}{d_E} \quad (8)$$

where d_{BPE} is the length of bipolar electrode. The value of ΔV_{BPE} was stable for the time scale of the electrolysis.

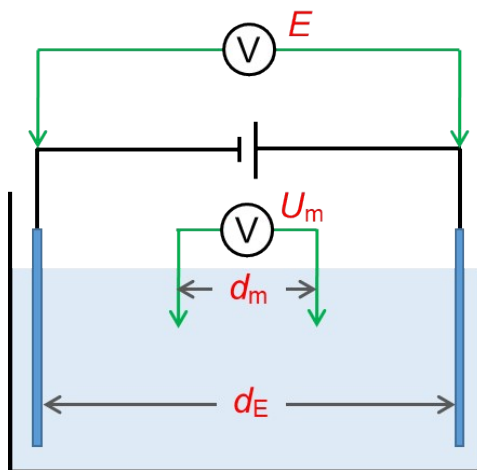


Fig. S4 Cell configuration and definition of the parameters for the equations.

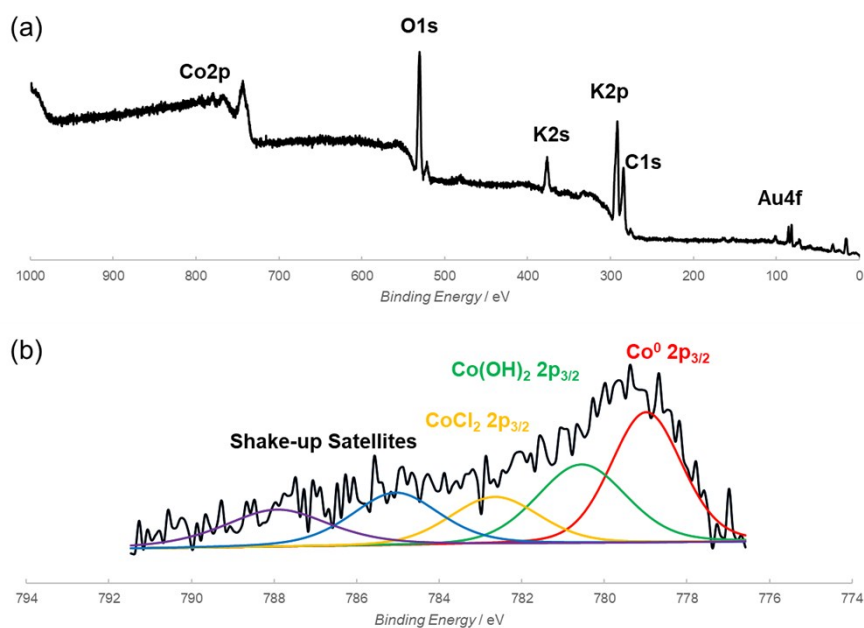


Fig. S5 (a) XPS survey spectra for Co nanorods. (b) Deconvoluted Co2p XPS spectrum for Co nanorods.

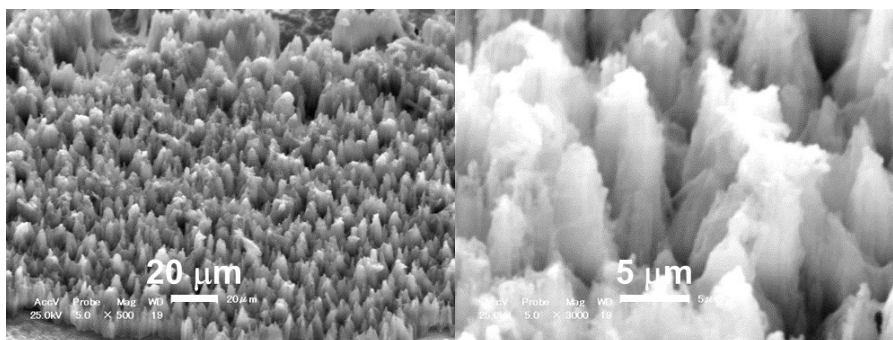


Fig. S6 SEM images of Co nanotubes prepared by the template-based constant potential electrolysis in a conventional manner.

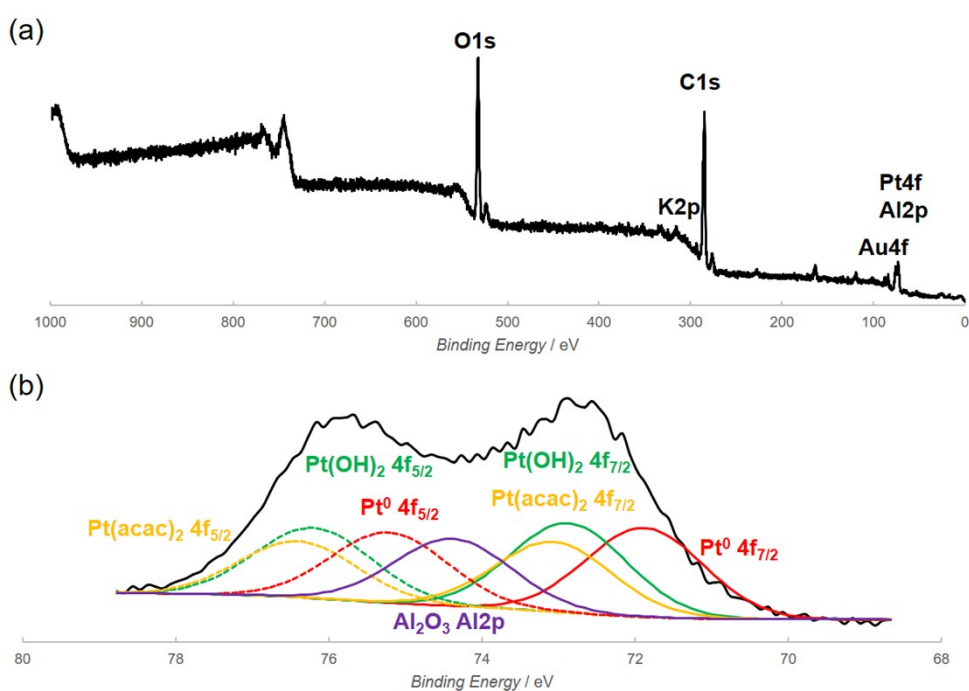


Fig. S7 (a) XPS survey spectrum for Pt nanorods. (b) Deconvoluted Pt4f XPS spectrum for Pt nanorods.

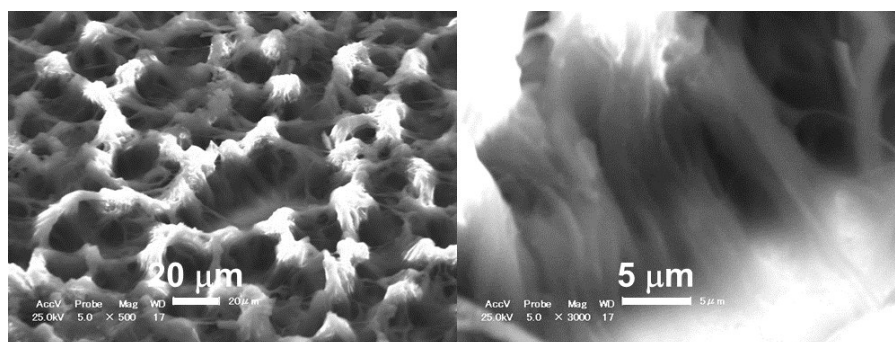


Fig. S8 SEM images of Pt nanotubes prepared by the template-based constant potential electrolysis in a conventional manner.

References

1. G. Loget, J. Roche and A. Kuhn, *Adv. Mater.*, 2012, **24**, 5111–5116.
2. Y. Koizumi, N. Shida, I. Tomita and S. Inagi, *Chem. Lett.*, 2014, **43**, 1245–1247.