Supplementary Material (ESI) for Chemical Communications

Perpendicular mesoporous Pt thin films: electrodeposition from titania nanopillars and their electrochemical properties

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Contents

SI. 1. Characterization of the Titania Template

i) Diffusion in the titania template.

Anion species of Pt, $PtCl_6^{2-}$, is generally applied for electrodepositing Pt, while anion diffusion among titania nanostructure was reported to be limited by electrostatic expulsion of negative charged titania surface. Thus, we evaluated the possibility of anion diffusion in our titania template by cyclic voltammetry (CV) in 1 mM $K_3[Fe(CN)_6]$ (containing 100 mM Na_2SO_4) at 30°C.

CVs of $Fe(CN_6)^{3-}$ on different electrodes modified with nanostructured titania are shown in Fig. S1: (a) ITO electrode, (b) Pt electrode. Only redox reaction of $Fe(CN_6)^{3-}$/ $Fe(CN_6)^{4-}$ was observed in the CVs, and moreover peak currents are the same between electrodes with and without modification. That is, the titania does not work as electrode in this condition.

Diffusion limiting current density on the ITO electrode modified with the nanostructured titania calcined at 400°C (blue line) is obviously larger than that at 200°C (red line). Probably, the structure change to the nanopillars drastically increase the mass transfer inside the titania film.

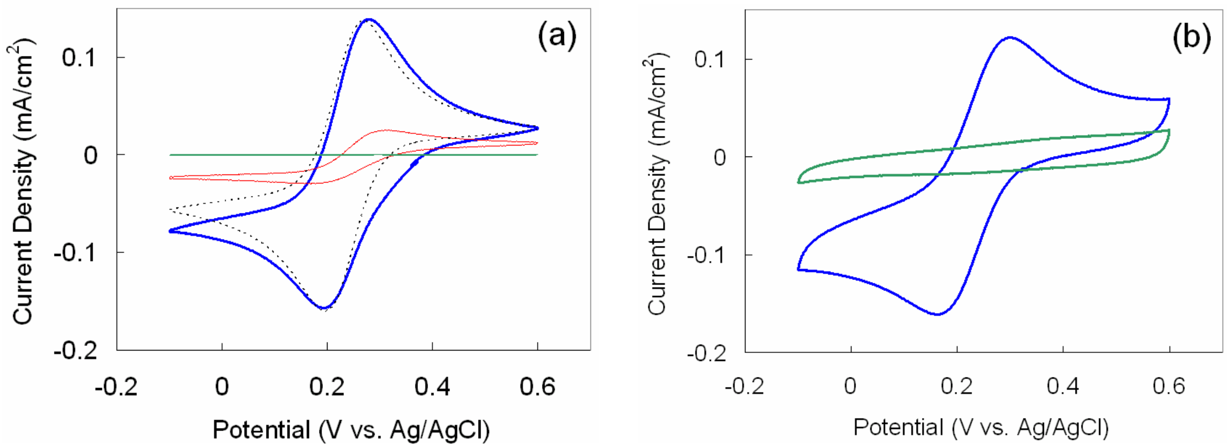

Figure S1. Cyclic voltammogramms of 1 mM $Fe(CN)_6^{3-}$ at 30°C on different electrodes modified with the nanostructured titania: (a) ITO substrate, (b) Pt substrate. Blue line: with nanostructured titania calcined at 400°C (nanopillars); Red line: with nanostructured titania calcined at 200°C; Dotted line: a bare substrate heated at 400°C; Green line: voltammogram without $Fe(CN)_6^{3-}$.

ii) CV of the Pt electrode modified with titania nanopillars.

CV of the Pt electrode modified with nanostructured titania nanopillars is compared to that of a Pt electrode in Fig. S2. CV of the modified Pt is not the same as a pure Pt electrode. In double-layer region, current (0.2–0.3 V) is almost the same, while, in oxide region (0.4–1.0 V) and hydrogen region(-0.2–0.2 V), current is different. Thus, the Pt substrate of the template is found to be influenced by the modification of titania.

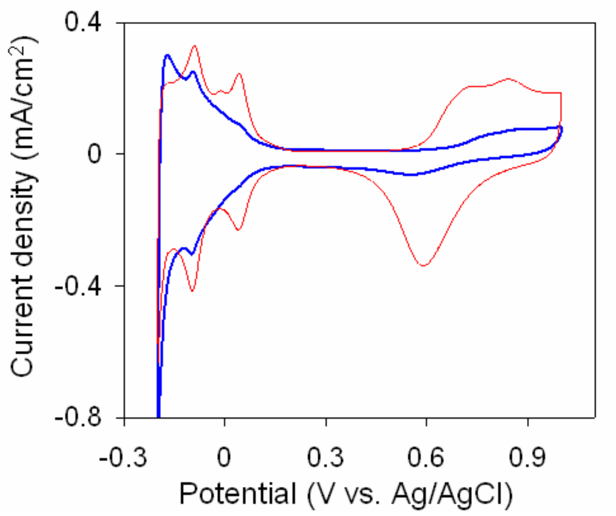

Figure S2. Cyclic voltammograms of the Pt electrode modified with nanostructured titania calcined at 400˚C (blue line) and a polished Pt electrode in 0.5 M sulfuric acid saturated with nitrogen.

iii) Porosity of the titania nanopillars.

Porosity of the mesoporous titania template (nanopillars) was evaluated by water vapor adsorption-desorption isothermal line. Film thickness, porosity, and pore size of the mesoporous titania films were determined by using an environmental ellipsometric porosimetry (EEP) device. Water vapor was used as an adsorption-desorption gas, and the measurement was performed at ambient pressure and temperature. More detailed experimental conditions (the setting of the film samples and the analysis of the obtained data) are described in a previous paper by Sanchez's group (*Langmuir* **2005**, *21*, 12362).

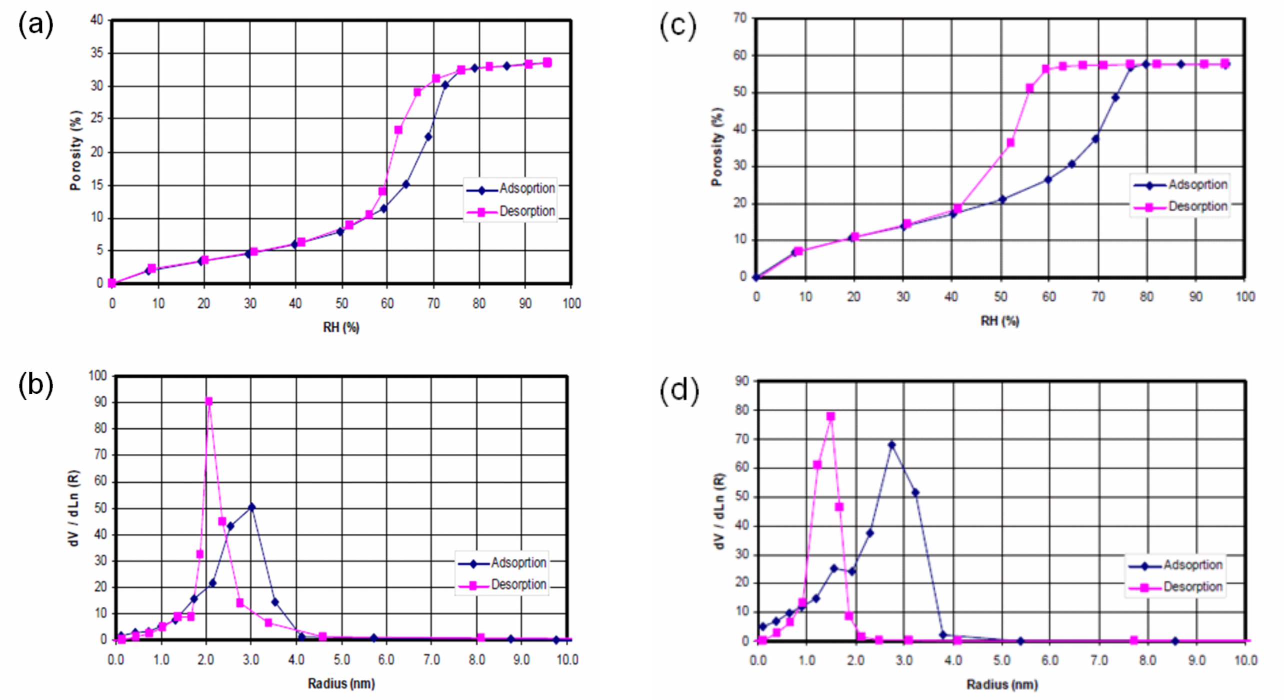

Figure S3. Steam absorption isothermal lines of the nanostructured titania calcined at 200˚C (a) and 400˚C (b). Corresponding pore distribution lines of 200˚C (b) and 400˚C (d).

Table S1. Porosity of the Nanostructured Titania Film Calcined at Different Temperature

	open porosity (%)	mean pore radius (nm)	mean interconnection dimension (nm)	thickness (μm)
400˚C	33.5	3.0	2.1	173
200˚C	57.6	2.7	1.5	438

iv) SEM images of mesoporous titania calcined at 200°C .

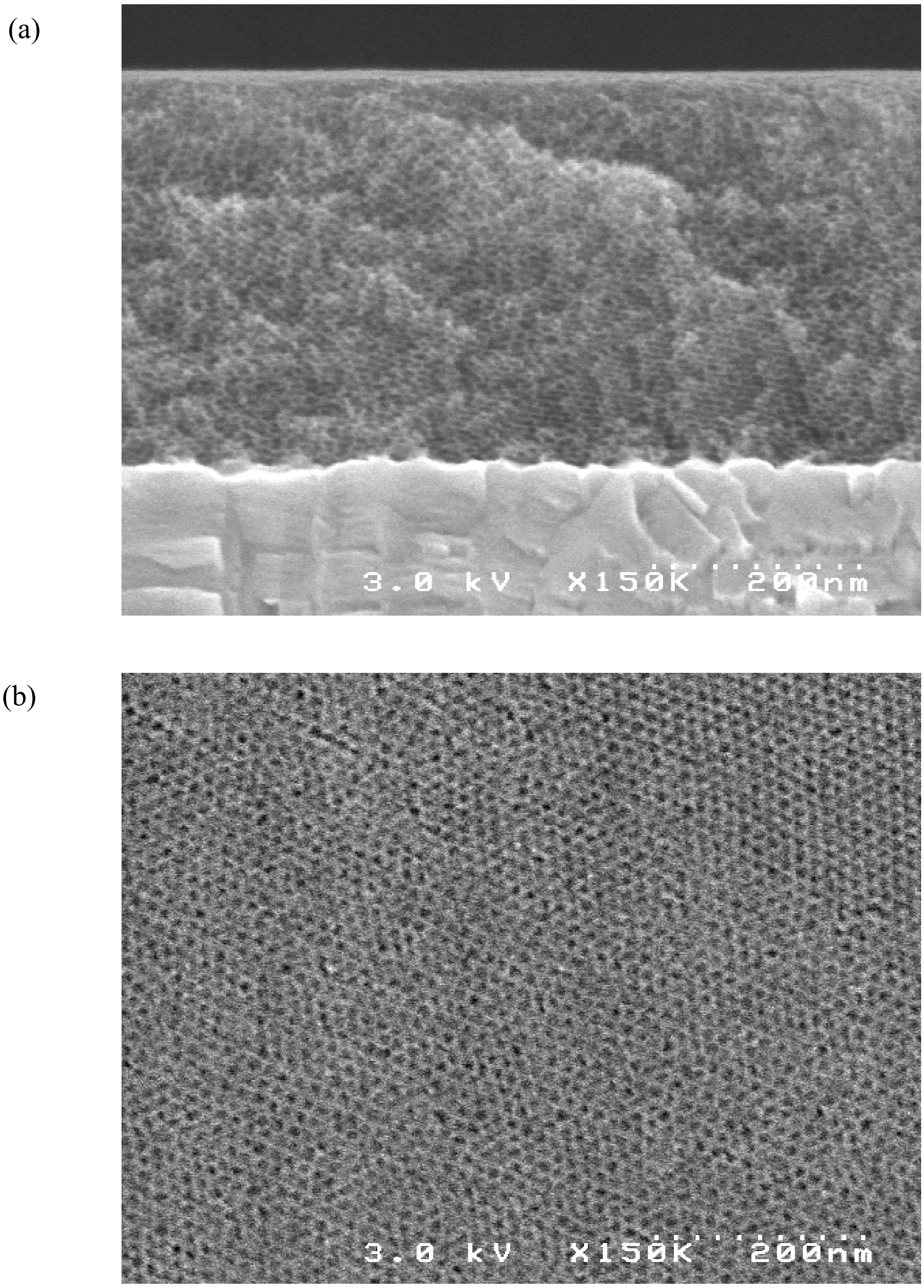

Figure S4. SEM images of a mesoporous titania film on an ITO substrate after calcined at 200°C. (a) Cross-sectional view, and (b) Top view.

SI. 2. Observation of the mesoporous Pt

i) SEM observation of the mesoporous Pt.

The synthesized mesoporous Pt is observed using SEM (Hitachi, S6500) (Fig. S5). This image indicates perpendicular pores well. This sample for cross-sectional observation was prepared by simple physical cracking method. On the surface, this sample possessed over-filled Pt, which probably protect the fine structure from breaking as shown in Fig. 2.

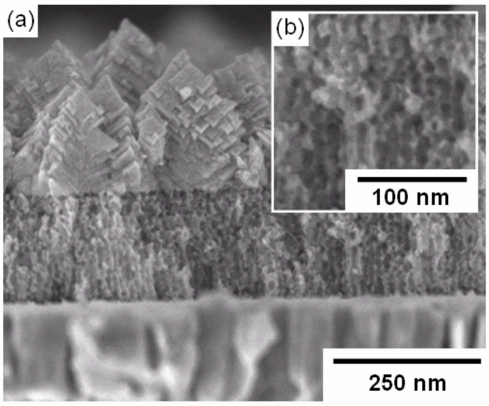

Figure S5. SEM images of a mesoporous Pt synthesized using the titania-pillars template under steady state electrodeposition. (S6500, Hitachi).

i) TEM observation of the mesoporous Pt.

The synthesized mesoporous Pt is also observed using high-resolution TEM (HR-TEM, Hitachi, H-9000NAR) at 300 kV (Fig. S6), and the TEM images displays Pt nanocrystallites with sizes of 5–7 nm. In this case, the observed sample was prepared through focused ion beam (FIB) process (Hitachi, FB2100) at 40 kV (0.01 nA) followed by ion thining process (GATAN, PIPS) at 3–4 kV (1 mA). The low magnified view of the TEM image and the corresponding SEM image are show in Fig. S7. Elemental mapping of Pt and Ti were obtained using TEM-EDX as show in Fig. S8.

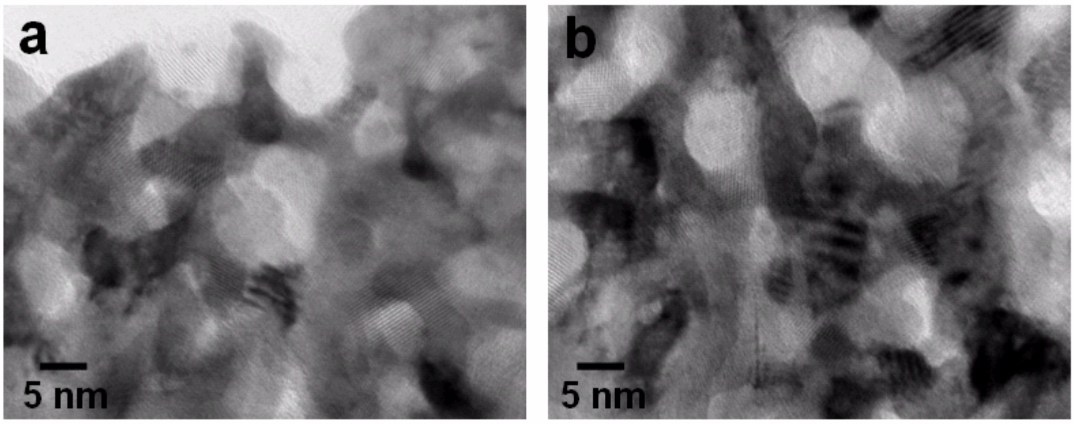

Figure S6. High resolution transmission electron microscopy (HR-TEM) images of the mesoporous Pt synthesized using titania pillars as a template.

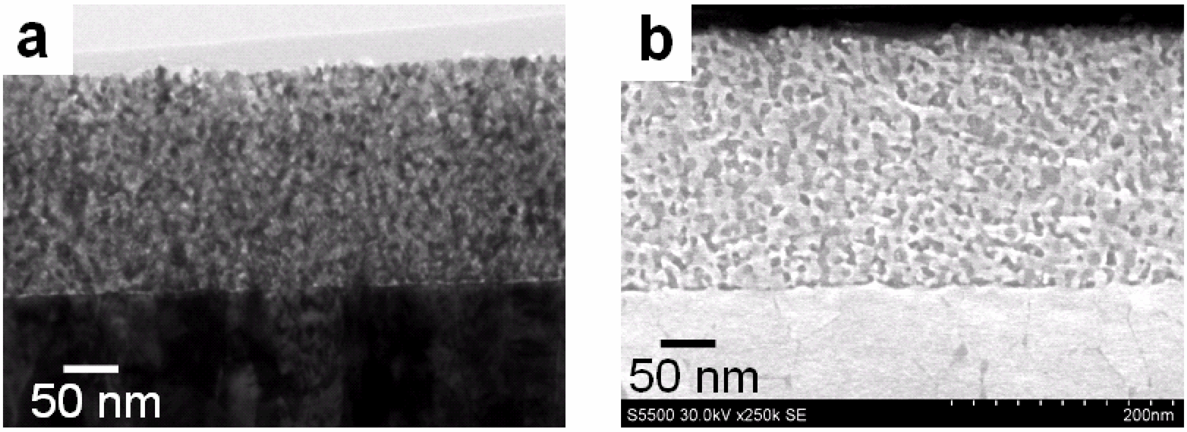

Figure S7. Comparison of the microscope images of the mesoporous Pt after FIB process: (a) TEM image and (b) SEM image.

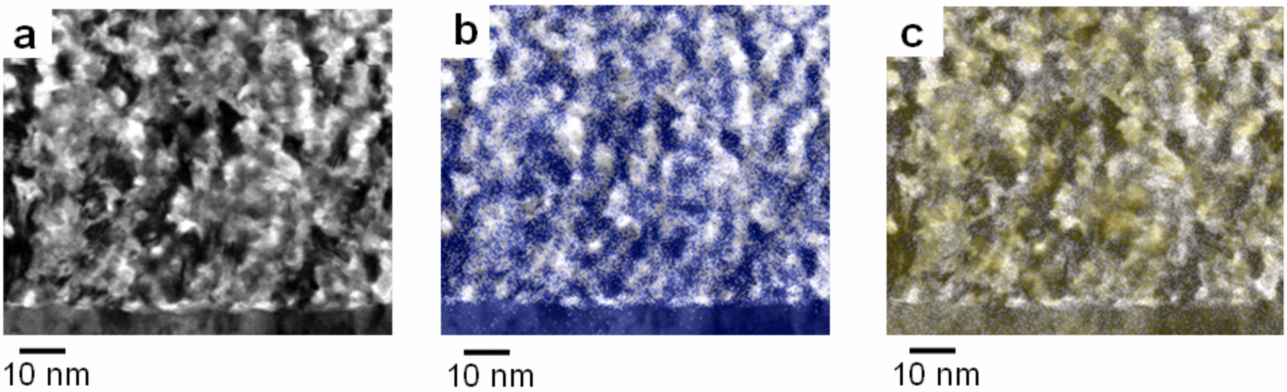

Figure S8. Elemental mapping obtained by TEM-EDX: (a) STEM image, (b) STEM image with EDX mapping of Pt-L, and (c) STEM image with EDX mapping of Ti-K.

SI. 3. Analyses on the CV of Pt electrodes

CV of the mesoporous electrode is shown in Fig. S9. The solid line means the CV of the mesoporous Pt. The dotted line means the CV of the Pt substrate of the template. The CV of the mesoporous electrode shows a typical response of a polycrystalline Pt in acid media; in addition, the response of the mesoporous electrode is much higher than that of the template. Thus, the prepared electrode was identified a polycrystalline Pt electrode with large surface area. Roughness factor, R_f, was estimated aS60.6 on the basis of the hydrogen desorption charge, Q_H (10.6 mC/cm^2), and 0.21 mC/cm^2 of the smooth Pt electrode.

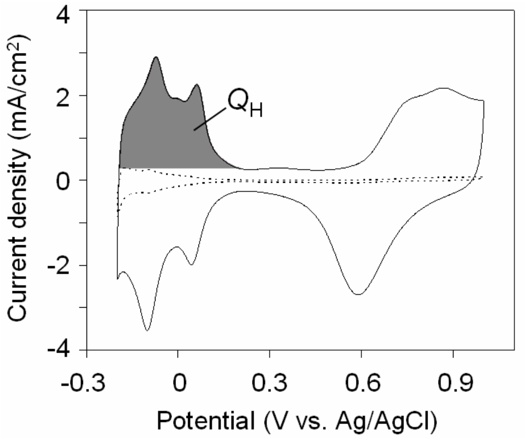

Figure S9. Cyclic voltammograms of the mesoporous Pt (solid line) in nitrogen saturated 0.5 M sulfuric acid solution at 50 mV/s. The dotted: CV of the Pt substrate modified with titania nanopillars (template).