Supporting Information

Open Pore Architecture of an Ordered Mesoporous IrO$_2$ Thin Film for Highly Efficient Electrocatalytic Water Oxidation

Debraj Chandra,*[a] Naoto Abe,[a] Daisuke Takama,[a] Kenji Saito,[a] Tatsuto Yui,[a] and Masayuki Yagi*[a, b]

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Detailed Experimental

Materials: Potassium hexachloroiridate(IV) (K$_2$IrCl$_6$) and sodium hydroxide (NaOH) were obtained from Wako Chemical Co. Triblock copolymer Pluronic F127 was purchased from Sigma-Aldrich. The F-doped tin oxide (FTO) glass substrate was obtained from Asahi Glass Co. All the chemicals of analytical grade were used as received. All the solutions were prepared with Millipore water.

Synthesis of 2D Hexagonal Mesoporous IrO$_2$ Electrodes: In a typical synthesis, 0.12 g of Pluronic F127 was dissolved in 2 mL of a 0.1 M aqueous NaOH solution, and then to the solution was slowly added 0.10 g (0.21 mmol) of K$_2$IrCl$_6$ under vigorous stirring at 50 ºC. After stirring for 15 min, the initial dark brown solution changed to light amber in color due to hydrolysis of an Ir-precursor (basic hydrolysis procedure). After stirring (30 min ~ 24 h; typically 30 min for optimized synthesis) at room temperature, the resultant homogeneous solution was spin-coated on a FTO substrate with a spinning rate of 3000 rpm. Before spin-coating, the FTO substrate was cleaned up by a UV-ozone treatment (SEN LIGHTS Co. Photo Surface Processor PL16-110) for 15 min and the coated area was fixed to be 0.8×1.25 cm. The as-coated film was dried at 80 ºC for 15 min, and annealed at 150 ºC for 20 min. After repeating the procedure for 2 times, the electrode was heated at 400-500 ºC (1 ºC min$^{-1}$) in flowing N$_2$ and maintained at these temperatures for 1 h, followed by calcination at these temperatures for 3 h in flowing O$_2$. After cool down to room temperature the IrO$_2$-coated substrate was washed by copious amount of water and dried in air. The resultant sample was denoted as mesoporous-IrO$_2$. The control sample was prepared under the identical synthesis procedures except the addition of Pluronic F127, denoted as untemplated- IrO$_2$.

Structural Characterization: Characterization of the mesoporous structures and the crystalline phase were conducted by transmission electron microscopy (TEM; JEOL 2010, operated at 200 kV) and powder X-ray diffraction (XRD; Rigaku MiniFlexII and Bruker AXS D8 Advanced SWAX diffractometer) using monochromated Cu Kα (λ = 1.54 Å) radiation, respectively. The TEM images and XRD data were taken of powders scratched off from the calcined films on the glass substrate. The surface morphology and film thickness were observed by scanning electron microscopy (SEM; JEOL JSM-6500F). Kr adsorption-desorption isotherms were obtained by using a Quantachrome Autosorb-1C at 87K of liquid Ar. The calcined films on glass with a total area of ca. 100 cm$^2$ were introduced into an exclusive sample cell and degassed at 120 ºC for 6 h under vacuum. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the surface areas. The film thicknesses were measured by using a KLA-Tencor-P-15 surface profiler. Thermogravimetric (TG) analysis was carried out using a Rigaku TG 8120 analyzer from 25 to 800 ºC with a heating rate of 5 ºC min$^{-1}$ under air. The XPS spectra were recorded using a JEOL JPS-9000 and calibrated by Au4f$_{7/2}$ peak, appeared at 83.0 eV. Raman spectra were recorded using a Raman spectrophotometer (a Horiba-Jobin-Yvon LabRAM HR) using 532 nm excitation and silicon standard wavenumber (520.7 cm$^{-1}$). For analysis of the iridium amount, IrO$_2$ films on FTO electrode was dissolved in an aqua regia and the iridium amount in the dissolved solution was measured using an inductively coupled plasma mass (ICP-MS) spectrometer (Yokogawa, HP4500).

Electrochemical Measurements: Electrochemical measurements were carried out using an electrochemical analyzer (Hokuto HZ-3000). A two-compartment electrochemical cell separated by a Nafion membrane was used. A three-electrode-type system has been employed by using an IrO$_2$-coating FTO electrode as working electrode and an Ag/AgCl reference electrode in one
compartment and a Pt wire counter electrode in the other compartment. An aqueous 0.1 M phosphate buffer solution (PBS, pH ≈ 7) was used as an electrolyte in both the compartment of electrochemical cell, which was sealed and saturated with Ar gas prior to the electrochemical measurement. The cyclic voltammograms (CV) were recorded at a scan rate of 50 mV s$^{-1}$ between the ranges of 0 V and 1.5 V at 25 ºC. Tafel plots were derived using a linear sweep voltammogram (LSV) measured at a scan rate of 0.5 mV s$^{-1}$ between the ranges of 0.8 V and 1.1 V. Electrochemical impedance spectra were measured at an applied potential of 0.9 V vs SCE in PBS of pH ≈ 7 in a frequency range of 100 mHz to 20 kHz (amplitude of 10 mV) using the electrochemical analyzer controlled by a frequency response analyzer (NF Electronic Instruments, S-5720C). To detect the H$_2$ and O$_2$ gasses evolved during electrocatalysis, the reaction cell was purged by Ar gas for 1 h prior to electrocatalysis to remove residual air. The electrolyte in the working compartment was 5 mL and the headspace volume was 87.3 mL. Electrocatalytic water oxidation was conducted at 1.2 V vs Ag/AgCl of applied potential for 1 h, and the current was recorded during the course of electrolysis by the electroanalyzer. The amounts of H$_2$ and O$_2$ evolved during electrocatalysis were analyzed in the gas phases (headspace regions) of counter and working electrode compartment, respectively on a gas chromatograph (Shimadzu, GC-8A with TCD detector and molecular sieve 5A column and Ar carrier gas).
Table S1. Physicochemical properties of different mesoporous- and untemplated-IrO₂ films.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Calcination temperature</th>
<th>d-spacing ( ^a ) [nm]</th>
<th>Surface area ( ^b ) [m(^2)cm(^-2)]</th>
<th>Surface area ( ^b ) [m(^2)g(^-1)]</th>
<th>Pore volume ( ^b ) [cm(^3)cm(^-3)]</th>
<th>Thickness [nm]</th>
<th>Coverage ( ^c ) [mol(^\text{cm}^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous-IrO₂</td>
<td>As-made</td>
<td>15.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>105</td>
<td>3.3 ( \times ) 10(^8)</td>
</tr>
<tr>
<td>Mesoporous-IrO₂</td>
<td>400 °C</td>
<td>13.9</td>
<td>512</td>
<td>105</td>
<td>0.58</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Mesoporous-IrO₂</td>
<td>450 °C</td>
<td>12.6</td>
<td>482</td>
<td>90</td>
<td>0.54</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>Mesoporous-IrO₂</td>
<td>500 °C</td>
<td>11.9</td>
<td>338</td>
<td>65</td>
<td>0.55</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>Untemplated-IrO₂</td>
<td>400 °C</td>
<td>–</td>
<td>45</td>
<td>4</td>
<td>0.04</td>
<td>93</td>
<td>3.2 ( \times ) 10(^4)</td>
</tr>
</tbody>
</table>

\( ^a \) \( d \)-spacings were calculated from the maxima of the small angle XRD patterns; \( ^b \) Calculated considering the pore volume and the density of crystalline IrO₂ of 11.66 g cm\(^{-3}\); \( ^c \) Coverage is measured by an inductively coupled plasma mass spectrometry (ICP-MS) technique.

Table S2. Summary of data on electrocatalytic water oxidation at 1.2 V vs Ag/AgCl for 1h using different mesoporous- and untemplated-IrO₂ films.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Calcination temperature</th>
<th>Charge / C</th>
<th>( n_{\text{O}_2} ) [( \mu )mol]</th>
<th>( \text{FE}_{\text{O}_2} ) ( ^a ) [%]</th>
<th>( n_{\text{H}_2} ) [( \mu )mol]</th>
<th>( \text{FE}_{\text{H}_2} ) ( ^c ) [%]</th>
<th>( R_{\text{mes}} ) ( ^d )</th>
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<tbody>
<tr>
<td>Mesoporous-IrO₂</td>
<td>400 °C</td>
<td>4.81</td>
<td>10.7</td>
<td>96</td>
<td>21.3</td>
<td>85</td>
<td>2.0</td>
</tr>
<tr>
<td>Mesoporous-IrO₂</td>
<td>450 °C</td>
<td>3.60</td>
<td>9.3</td>
<td>100</td>
<td>18.7</td>
<td>100</td>
<td>2.6</td>
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<tr>
<td>Mesoporous-IrO₂</td>
<td>500 °C</td>
<td>1.76</td>
<td>4.4</td>
<td>96</td>
<td>8.6</td>
<td>94</td>
<td>1.7</td>
</tr>
<tr>
<td>Untemplated-IrO₂</td>
<td>400 °C</td>
<td>2.13</td>
<td>5.3</td>
<td>97</td>
<td>10.2</td>
<td>93</td>
<td></td>
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<tr>
<td>Untemplated-IrO₂</td>
<td>450 °C</td>
<td>1.38</td>
<td>3.6</td>
<td>100</td>
<td>7.2</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Untemplated-IrO₂</td>
<td>500 °C</td>
<td>1.00</td>
<td>2.6</td>
<td>95</td>
<td>4.3</td>
<td>84</td>
<td></td>
</tr>
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</table>

\( ^a \) \( \text{FE}_{\text{O}_2} \) is Faraday efficiency for O\(_2\) evolution; \( ^b \) \( n_{\text{H}_2} \) is the amount of H\(_2\) during the electrocatalysis; \( ^c \) \( \text{FE}_{\text{H}_2} \) is Faraday efficiency for H\(_2\) evolution; \( ^d \) \( R_{\text{mes}} \) was defined as ratio of the amounts (\( n_{\text{O}_2} \)) of O\(_2\) evolved for mesoporous- and untemplated-IrO₂ at corresponding calcination temperature.

Table S3. Parameters of the elements in the equivalent circuit for fitting impedance data at 0.9 V vs SCE of mesoporous- and untemplated-IrO₂ films calcined at 400 °C.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>( R_{\text{ct}} ) / Ω</th>
<th>( R_{\text{it}} ) / Ω</th>
<th>CPE ( T_{\text{CPE}} ) / µF</th>
<th>CPE ( p )</th>
<th>( Z_{\text{w}} ) ( ^a ) / Ω</th>
<th>( Z_{\text{w}} ) ( ^b ) / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous-IrO₂</td>
<td>96.0</td>
<td>25.8</td>
<td>430</td>
<td>0.78</td>
<td>152</td>
<td>45</td>
</tr>
<tr>
<td>Untemplated-IrO₂</td>
<td>96.0</td>
<td>42.0</td>
<td>122</td>
<td>0.82</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\( ^a \) \( T_{\text{CPE}} \) is CPE constant; \( ^b \) \( p \) is CPE exponent of non-ideality; \( ^c \) \( Z_{\text{w}} \) is Warburg impedance; \( ^d \) \( Z_{\text{w}} \) (R) is diffusion resistance.
Figure S1. TEM images of mesoporous-IrO$_2$ films calcined at (a) 450 °C and (b) 500 °C.

Figure S2. XPS spectra of the Ir4f region of mesoporous-IrO$_2$ films calcined at 400 °C, 450 °C and 500 °C.
**Figure S3.** Raman spectra of the precursor film (a) and the mesoporous-IrO$_2$ films calcined at 400 °C (b) and 500 °C (c).

**Figure S4.** TG analysis curves started with powder samples recovered by scratching of the as-prepared films for (a) untemplated- and (b) mesoporous-IrO$_2$ under air with a heating rate of 5 °C min$^{-1}$.
Figure S5. Photographs of mesoporous-IrO$_2$ films calcined at 400 °C, 450 °C and 500 °C.

Figure S6. TEM (a) and SEM (b) images of the IrO$_2$ film prepared without using F127 and calcined at 400 °C.
Figure S7. Small-angle XRD patterns of IrO$_2$ films prepared without using F127 for as-made and after being calcined at 400 °C.

Figure S8. Wide-angle XRD patterns of powder samples recovered by scratching of mesoporous-IrO$_2$ films for as-made and after being calcined at 400 °C, 450 °C and 500 °C.
Figure S9. Kr adsorption-desorption isotherm of the IrO$_2$ film prepared without using F127, followed by calcination at 400 °C. Adsorption points are marked by closed symbols and those for desorption by opened symbols.

Figure S10. Tafel plots for electrocatalytic water oxidation in a 0.1 M phosphate buffer solution (pH = 7) for IrO$_2$ electrodes calcined at 400 °C. η is an overpotential for O$_2$ evolution and calculated from the difference between the applied potential and the theoretical (0.618 V vs Ag/AgCl) potential for O$_2$ evolution at pH = 7.
Figure S11. Nyquist plots (left) for mesoporous- and untemplated-IrO₂ electrodes calcined at 400 °C as measured in a 0.1 M phosphate buffer solution (pH ≈ 7) at 0.9 V versus SCE. The solid lines show the simulated spectra using the equivalent circuits (right) for fitting the impedance data. $R_{ct}$, $R_{sol}$, $Z_w$ and CPE are charge transfer resistance, solution phase resistance, Warburg impedance and constant phase element, respectively.

Figure S12. Cyclic voltammograms (left) and current-time profiles (right) during electrocatalysis using the mesoporous-IrO₂ electrodes calcined at 400 °C, 450 °C and 500 °C as measured in a 0.1 M phosphate buffer solution (pH ≈ 7) at 1.2 V versus Ag/AgCl.