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Electrocatalytic activity of electrodeposited cobalt oxide-modified to produce oxygen gas from water

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Abstract

An electrocatalytic cobalt oxide film for water oxidation was prepared on an indium tin oxide (ITO)-coated substrate by anodic electrodeposition. Atomic force microscopy measurements revealed that numerous particles with a diameter of 100–250 nm were uniformly dispersed on the ITO substrate and the particle size increased when prepared at higher temperature. Cyclic voltammograms of the Co oxide-coated ITO electrodes were measured in alkaline and neutral aqueous solutions to examine their redox characteristics and ability to catalyze water oxidation. When Co oxide was electrodeposited from solutions kept at 10, 25 and 50 °C, the amount of electroactive Co oxide per unit area (Γ_{ea}) was 1.06×10^{-8} , 1.72×10^{-8} , and 2.31×10^{-8} mol cm⁻², respectively. The increase in Γ_{ea} accompanied the increase in particle size observed with rising deposition temperature. Quantitative analyses of O₂ gas produced by water electrolysis were carried out under potentiostatic conditions using these Co oxide-modified electrodes and a bare ITO electrode for comparison. For the Co oxide-coated electrode prepared at 10 °C, the amount of O₂ evolved by electrolysis for 2 h at 1.3 V vs. Ag/AgCl was 1.3×10^{-5} mol cm⁻² in alkaline electrolyte solution and 1.52×10^{-5} mol cm⁻² in neutral electrolyte solution containing phosphate ions. In addition, when the Co oxide-coated electrode treated at 450 °C was used, the amount of O₂ evolved by the electrolysis increased to 2.58×10^{-5} mol cm⁻² in the neutral electrolyte solution containing phosphate ions, resulting from a stable catalytic current.

Keywords: Water oxidation, Cobalt oxide, electrochemical deposition, electrochemical catalysis, pH dependency, electrolyte dependency

Introduction

Effective and cheap catalysts for O_2 evolution by water oxidation (Eq.: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) are needed for the development of industrial electrochemical processes as well as artificial photosynthetic devices to provide a socially acceptable renewable energy source. Converting water to O_2 and H_2 is a major subject for developing energy conversion systems that store renewable resources in the form of chemical fuels. Conductive metal oxides have been used as water oxidation catalysts in electrolyzers for many decades. It is well known that metal oxides such as RuO_2 , IrO_2 and Co_3O_4 have catalytic activities for water oxidation.[1-4] In our previous studies, we prepared IrO_2 nanoparticle- and colloid-coated electrodes by electrodeposition and self-assembly which revealed high catalytic-activity for water electrolysis.[5-7] However, although RuO_2 and IrO_2 are the high-active catalyst, their noble metals are rare materials on earth and are not suitable for use on a very large scale. Therefore, it is important to develop other oxide catalysts using more abundant transition metals. Cobalt (Co) oxide catalysts have been attracting much attention as a promising candidate for photo- [8, 9] and electrocatalysis [10-21] of water oxidation. Recently, Kanan and Nocera [22] reported a cobalt-phosphate (Co-Pi) catalyst for water oxidation. Their Co-Pi catalyst not only exhibited high activity but also a self-healing feature that suppressed release of Co^{2+} ions into solution during water-splitting catalysis.[23, 24] Herein we report the characterization of Co oxide films prepared from a citrate-cobalt complex by electrodeposition, and determine the electrocatalytic activity of the Co oxide catalysts based on the amount of O_2 evolved. It is found that

the catalytic activity decreases with increasing deposition temperature, possibly because of the increased particle size.

2. Experimental Section

2.1. Materials

Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), potassium nitrate (KNO_3), sodium dihydrogen phosphate dihydrate, and disodium hydrogen phosphate 12-water were purchased from Kanto Chemical Co. Ltd. Sodium hydrogen citrate sesquihydrate was purchased from Aldrich Chemical Co. Inc. All chemicals were the purest grade available, and used as received. Glass-indium tin oxide (ITO) substrates (sheet resistance = $10 \text{ } \Omega/\text{sq}$) were purchased from Furuuchi Chemical Co.

2.2. Preparation of cobalt oxide films on ITO electrodes

The glass-ITO electrodes were first cleaned by sonication in 2-propanol, washed in boiling 2-propanol, and then dried in air. Cobalt oxide-coated ITO electrodes were prepared by the method reported by Casella.[25] $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (45.2 mg, $1.9 \times 10^{-4} \text{ mol}$) was added to an aqueous solution (50 mL) of sodium hydrogen citrate sesquihydrate (50 mg, $1.9 \times 10^{-4} \text{ mol}$), where the citrate ions acted as ligands for Co^{2+} ions to prevent the precipitation of $\text{Co}(\text{OH})_2$ in alkaline solution. This pale-red solution was adjusted to pH 11.0 with 0.25 M NaOH solution. KNO_3 was added as a supporting electrolyte to the pale-red solution. The solution was diluted to 100 mL and then re-adjusted to pH 11.0. The aqueous solution containing 1.9 mM CoCl_2 , 1.9 mM sodium hydrogen citrate, and 0.1 M KNO_3 was used as an electrolytic solution to prepare Co oxide-modified ITO electrodes under the potentiostatic conditions of 0.85 V vs. Ag/AgCl . Three modified electrodes with an effective area of

1.0 cm² were prepared from electrolytic solutions at temperatures of 10, 25, and 50 °C, where the amount of the charge passed was 0.15 C cm⁻². A conventional single-compartment electrochemical cell was used for the anodic electrodeposition, where ITO was employed as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the counter electrode.

2.4. Measurements

UV-visible absorption spectra were measured by a spectrophotometer (Hitachi, U-3310). X-ray diffraction (XRD) measurements were carried out using an X-ray diffractometer (Rigaku, RINT 2500), and atomic force microscope (AFM) images were recorded using an AFM (SII, SPI3800N). To characterize the Co-oxide modified ITO electrodes, cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out at a scan rate of 20 and 0.5 mV s⁻¹, respectively, in aqueous solutions at pH 7.0 and 11.6 containing various electrolytes. Experiments to electrochemically produce O₂ gas from water were conducted in 0.1 M KNO₃ solution at pH 11.6 and in 0.05 M phosphate solution at pH 7.0, using a gas-tight single-compartment cell equipped with a modified ITO working electrode, Ag/AgCl reference electrode, and platinum-wire counter electrode. Water electrolysis was performed for 2h by applying a constant potential in the range of 0.5 to 1.3 V vs. Ag/AgCl to the modified electrode. The gas evolved by electrolysis was analyzed by a gas chromatograph (Shimadzu, GC-8APT) equipped with a molecular sieve 5 Å column using argon as a carrier gas (flow rate: 40 cm³/min) at 80 °C. All electrochemical experiments were

implemented under an argon atmosphere at 25 °C using an electrochemical analyzer (Hokuto Denko, HZ-5000). The amount of Co atoms electrodeposited on ITO was estimated by quantitatively determining the concentration of Co ions eluted in nitric acid solution by inductively coupled plasma atomic emission spectrometry (ICP-AES) [6, 26].

3. Results and discussion

3. 1. Electrochemical catalytic activity in alkaline aqueous solution

A transparent ITO electrode modified with Co oxide was obtained by anodic deposition of over 0.8 V *vs.* Ag/AgCl in the pale-red solution described above at pH 11.0. We inferred the following deposition mechanism: First, citrate-coordinated Co^{2+} ions were oxidized on the ITO anode to Co^{3+} species by applying a potential of over 0.8 V. Next, the Co^{3+} species were hydrolyzed irreversibly accompanied by a polymerization reaction, releasing the citrate ions at the same time. This resulted in the deposition of an insoluble Co oxide on the ITO electrode. Surface AFM images of the Co oxide-coated electrodes (Fig. 1) showed that numerous particles with a diameter of 100–250 nm were uniformly dispersed over the ITO surface and the particle size increased when prepared from electrolytic solution at higher temperature. All of the Co oxide films were amorphous because their XRD patterns did not show any peaks originating from crystalline Co oxides.

Fig. 2(a) shows the CVs recorded in 0.1 M KNO_3 aqueous solution at pH 11.6 using the Co oxide-modified ITO electrodes deposited at different temperatures. Two reversible redox couples

with half-wave potentials of 0.15 and 0.3 V were observed. The couples are assigned as $\text{Co}^{\text{II}}(\text{OH})/\text{Co}_3\text{O}_4$ (that is, $\text{Co}^{\text{II}}\text{Co}_2^{\text{III}}\text{O}_4$) for the first wave and $\text{Co}_3\text{O}_4/\text{Co}^{\text{III}}\text{OOH}$ for the second, and hydroxyl ions may be involved in the electrochemical reactions. [27] Because the rest potential of the cobalt oxide film in alkaline solution showed 0.25-0.3 V, we assigned that deposited species is Co_3O_4 . The amount of electroactive Co oxide per unit area, denoted Γ_{ea} (mol cm^{-2}), was estimated from the area of the two anodic waves from 0.0 to 0.5 V in the CVs excluding the capacitive current area, because the passed charges were consumed by one-electron oxidation of Co^{II} to Co^{III} . When the Co oxide was deposited at 10, 25 and 50 °C by the constant amount of the passed charge of 0.15 C cm^{-2} , Γ_{ea} was 1.06×10^{-8} , 1.72×10^{-8} , and 2.31×10^{-8} mol cm^{-2} , respectively, as shown in Fig. 2(b); that is, Γ_{ea} increased with increase in the deposition temperature accompanying the increase in the particle size. When deposited at 10 °C, the coverage (Γ_{cov} (mol cm^{-2})) of Co atoms on the ITO electrode estimated by an ICP-AES technique was 7.54×10^{-8} mol cm^{-2} , so the fraction of Γ_{ea} to Γ_{cov} was ca. 14%.

Fig. 3a shows the CVs for the modified ITO electrodes in the range of 0 to 1.3 V vs. Ag/AgCl in 0.1 M KNO_3 aqueous solution at pH 11.6. When bare ITO was used as the working electrode, an onset potential was observed at 0.8 V for an irreversible anodic current. In contrast, when the Co oxide-modified ITO electrodes were used, two onset potentials were observed at 0.65 and 1.1 V for two irreversible anodic currents and the anodic peak current densities around 0.8 V exhibited ca. 1 mA cm^{-2} . When pH of the electrolytic solution turned into pH 11.9 and 11.3 that the concentration of

hydroxide ion was double and half from pH 11.6, respectively, the peak current densities around 0.8 V for the modified ITO electrodes deposited at 10 °C increased to 1.56 mA cm⁻² and decreased to 0.40 mA cm⁻² in response to the pH change, as shown in Fig. 3b. On the other hands, the current density over 1.1V, which showed gradually-increased with increase in the applied potential, was almost the same regardless of the pH change. This means that the oxidation rate was limited by a charge transfer process from the electrode to water molecules that are abundantly present. After all, the anodic peak around 0.8 V and the anodic response over 1.1 V were assigned to the oxidations of hydroxide ions and water molecules, respectively. In addition, the first onset potential of the Co oxide-modified electrodes shifted by 0.2 V toward the negative side compared with that of the bare ITO electrode.

Quantitative analysis of the O₂ gas produced by water electrolysis was carried out under potentiostatic conditions using the three Co oxide modified electrodes and a bare ITO electrode for comparison. Catalytic anodic currents were observed during electrolysis in 0.1 M KNO₃ aqueous solution at pH 11.6 under the potentiostatic conditions of 1.3 V *vs.* Ag/AgCl, as shown in Fig. 4. The amount of O₂ gas produced by electrolysis for 2 h is summarized in Table 1. The theoretical potential of water oxidation in this pH was 0.35 V *vs.* Ag/AgCl, and the overvoltage under electrolysis measurements was calculated with 0.95 V. The bare ITO electrode hardly functioned as a catalytic electrode for O₂ evolution by water electrolysis. But when the Co oxide modified electrode prepared at 50 °C was used, the amount of passed charge was 3.4 C cm⁻² and the amount of O₂ gas

produced was $8.6 \times 10^{-6} \text{ mol cm}^{-2}$. Furthermore, when the Co oxide-modified electrode prepared at 10 °C was used, the amount of passed charge was 5.4 C cm^{-2} and the amount of O₂ gas evolved was $1.3 \times 10^{-5} \text{ mol cm}^{-2}$. The Faradaic efficiency of 96.6% for the Co oxide-modified electrode prepared at 10 °C was similar to that of 97.2% for the Co oxide modified electrode prepared at 50 °C. These results show that the amount of O₂ produced by water electrolysis increased with a lower deposition temperature of the catalytic Co oxide. This is because the number of catalytic active sites for O₂ evolution per unit area; that is, the specific surface area of Co oxide increased as the particle size of the Co oxide deposited on the ITO electrode decreased. This result consists with AFM data as shown Fig. 1. In addition, the turnover frequencies (TOF) of the Co oxide deposited at 10 °C, 25 °C and 50 °C which defined as the amount (mol cm^{-2}) of O₂ gas evolved by the electrolysis per Γ_{ea} second ($\text{mol cm}^{-2} \cdot \text{s}$) were estimated to be 0.176 s^{-1} , 0.070 s^{-1} and 0.052 s^{-1} , respectively. This difference may be caused by reactive difference in amorphous state of Co oxide prepared at various temperatures.

The dependence of the amount of O₂ evolved using the Co oxide-modified electrode prepared at 10 °C on applied potential is shown in Fig. 5. The observed behavior was consistent with the LSV measurement scanned at 0.5 mV s^{-1} for the modified electrode that was indicated by a broken line. O₂ gas evolved by electrolysis for 2h was reliably detected at electrode potentials of over 0.6 V vs. Ag/AgCl, and the amount of O₂ was almost constant in the range of 0.7 to 1.1 V, whose values are equivalent to the overvoltage of 0.35 V to 0.75 V. This indicates that the reaction rate of

O₂ evolution was limited by the diffusion of hydroxide ions as the oxygen source. Furthermore, when a potential of over 1.1 V was applied, the amount of O₂ produced increased rapidly with electrode potential, suggesting that the reaction rate was determined by charge transfer to H₂O molecules as the oxygen source.

3. 2. Electrochemical catalytic activity in neutral aqueous solution

To evaluate the electrocatalytic activity of the Co oxide-modified electrode prepared at 10 °C in neutral aqueous solutions, CVs were measured in various aqueous solutions, as illustrated in Fig. 6. Because hydroxyl ions participating in the redox reactions are present in low concentration in 0.1 M KNO₃ and 0.05 M Na₂SO₄ solutions, small two oxidation peaks as shown in Fig. 6 of inset, which may be assigned as those of Co(OH)/Co₃O₄ and Co₃O₄/CoOOH couples, was observed at 0.4 and 0.9 V vs. Ag/AgCl, respectively, and then anodic current for water oxidation was observed over 1.2 V. On the other hand, the corresponding anodic peaks were observed at 0.65 and 0.8 V in 0.05 M phosphate solution. Then anodic current for oxygen evolution was observed over 1.0 V. This assignment is clarified by explanation of Fig. 7 later. However, when bare ITO was used as the working electrode in the phosphate solution, no anodic current was observed, even at an electrode potential of 1.3 V. These results suggest that the phosphate ions participated in the redox reactions observed using the Co oxide-modified electrodes.

The amount of O₂ gas evolved by electrolysis for 2 h in neutral aqueous solution containing phosphate buffer using the Co oxide-modified ITO electrode prepared at 10 °C is plotted against

applied potential in Fig. 7. O₂ gas evolved by electrolysis for 2h was reliably detected at electrode potentials over 1.2 V vs. Ag/AgCl, and its amount increased rapidly with increase in electrode potential. We inferred from these results that the Co oxide-modified electrode was an effective catalyst to produce O₂ from water only when Co species containing phosphate ions were further oxidized to species with a higher oxidation state.

Fig. 8 shows current-time curves for electrolysis under potentiostatic conditions of 1.3 V vs. Ag/AgCl in three electrolyte aqueous solutions at pH 7.0 using the Co oxide-modified electrode deposited on ITO at 10 °C. The theoretical potential of water oxidation in this pH was 0.62 V vs Ag/AgCl, and the overvoltage under electrolysis measurements was calculated with 0.68 V. When the electrolysis was carried out for 2 h in 0.1 M KNO₃ solution, the amounts of passed charge and O₂ gas evolved were 1.0 C cm⁻² and 3.5×10⁻⁷ mol cm⁻², respectively. Then, when the electrolysis was carried out for 2 h in 0.05 M Na₂SO₄ solution, the amounts of passed charge and O₂ gas evolved were 0.5 C cm⁻² and 3.1×10⁻⁷ mol cm⁻², respectively. Small Faradaic efficiencies of 12.9% and 24.9% were obtained in 0.1 M KNO₃ and 0.05 M Na₂SO₄, respectively. These small Faraday efficiencies suggest that the cathode undergoes an electrochemical backward reaction such as oxygen reduction, because oxygen evolution reaction rates are very slow. In contrast, when the electrolysis was carried out for 2 h in 0.05 M phosphate solution, the amount of passed charge was 8.7 C cm⁻² and that of O₂ gas evolved was 1.5×10⁻⁵ mol cm⁻², so the Faradaic efficiency was much higher at 87.9%. The amount of O₂ gas evolved was ca. 50 times higher in phosphate solution than in the two

other kinds of electrolyte solutions. The O₂ gas evolved in neutral electrolyte solution containing phosphate ions was higher than that (1.3×10^{-5} mol cm⁻²) in alkaline electrolyte solution, though the former overvoltage of 0.68 V was 0.27 V lower than the latter overvoltage of 0.95 V. In addition, O₂ gas evolved in alkaline solution were $4.9 \sim 5.6 \times 10^{-5}$ mol cm⁻² under overpotential of 0.55 ~ 0.75 V, and the O₂ gas evolved in neutral solution was 3 times higher than that in alkaline solution under nearly equal overpotential. In order to further improve the electrochemical catalytic activity of the modified electrodes, we attempted to prepare a Co oxide film with better crystallinity and grain boundary formation by heating treatment. Fig. 9 shows the current-time curves during electrolysis in phosphate buffer solution at pH 7.0 using a Co oxide-modified electrode treated at 450 °C. The constant anodic current density of over 2 mA cm⁻² was observed when the heating treated electrode was used, and the amount of O₂ gas evolved (2.58×10^{-5} mol cm⁻²) was ca. 1.7 times higher than when the as-prepared electrode was used. Due to no change of the XRD spectra and current density, this increase in O₂ evolution suggests that the heating treatment induces improvement of film durability by chemical bonding of inter-particle and particle-electrode surface rather than increase in crystallinity. Fig. 10 shows the surface AFM images of as-prepared and 450 °C heated Co oxide films. Decrease in surface roughness and sintering between the particles were observed after heating treatment. This result supports the above suggestion that increase in chemical bond-forming between the particles results in an improvement of catalytic activity for O₂ evolution.

Conclusion

Electrocatalytic water oxidation was demonstrated using an anodically electrodeposited Co oxide-coated ITO electrode. The amount of O₂ evolved by electrolysis for 2 h at 1.3 V vs. Ag/AgCl was 1.3×10^{-5} mol cm⁻² in alkaline electrolyte solution and 1.5×10^{-5} mol cm⁻² in neutral electrolyte solution containing phosphate ions, though the former overvoltage was 0.27 V lower than the latter overvoltage. In addition, the amount of O₂ gas evolved (2.6×10^{-5} mol cm⁻²) was ca. 1.7 times higher when the heating treated electrode was used than when the as-prepared electrode was used. A Co oxide film that can serve as an electrocatalyst for water oxidation is of great interest for designing anodes for industrial processes as well as catalytic systems for artificial photosynthetic devices.

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Table 1 Amount of O₂ produced by electrolysis in 0.1 M KNO₃ aqueous solution at pH 11.6 for 2 h under potentiostatic conditions of 1.3 V *vs.* Ag/AgCl.

Deposition temperature / °C	Amount of O ₂ produced / μmol cm ⁻²	Faradaic efficiency / %
10	13.4	96.6
25	8.7	89.2
50	8.6	97.2
bare ITO	0.12	8.3

Figure captions

Figure 1 Surface AFM images of (a) bare ITO and Co oxide-modified electrodes deposited at temperatures of (b) 10 °C, (c) 25 °C, and (d) 50 °C.

Figure 2 (a) Cyclic voltammograms of Co oxide-modified electrodes prepared at various temperatures in 0.1 M KNO₃ aqueous solution at pH 11.6 and a scan rate of 20 mV s⁻¹. The potential range was from -0.3 to 0.7 V vs. Ag/AgCl. (b) Dependence of the amount of electroactive Co oxide (Γ_{ea}) on electrodeposition temperature.

Figure 3 (a) Cyclic voltammograms of Co oxide-modified electrodes prepared at various temperatures in 0.1 M KNO₃ aqueous solution at pH 11.6. The potential range was from 0 to 1.3 V vs. Ag/AgCl. (b) Cyclic voltammograms of Co oxide-modified electrodes prepared at 10 °C in 0.1 M KNO₃ aqueous solution at pH 11.9, 11.6, and 11.3. The scan rate was 20 mV s⁻¹. The potential range was from 0 to 1.3 V vs. Ag/AgCl.

Figure 4 Current-time curves during electrolysis in 0.1 M KNO₃ aqueous solution at pH 11.6 under the potentiostatic conditions of 1.3 V vs. Ag/AgCl. The working electrodes were Co oxide-modified electrodes prepared at different temperatures and a bare ITO electrode.

Figure 5 Plots of the amount of O₂ evolved by electrolysis at various applied potentials for 2 h in 0.1 M KNO₃ aqueous solution at pH 11.6 using a Co oxide-modified electrode deposited at 10 °C. The broken line represents a linear sweep voltammogram of the Co oxide-modified electrode at a scan rate of 0.5 mV s⁻¹ in 0.1 M KNO₃ aqueous solution at pH 11.6.

Figure 6 Cyclic voltammograms of the Co oxide-modified electrode prepared at 10 °C in various electrolyte aqueous solutions at pH 7.0 and a scan rate of 20 mV s⁻¹. Inset illustrates the magnified figure of the voltammograms in KNO₃ and NaSO₄ solutions.

Figure 7 Plots of the amount of O₂ evolved by electrolysis at various applied potentials for 2 h in 0.05 M aqueous phosphate buffer solution at pH 7.0 using a Co oxide-modified electrode deposited at 10 °C. The broken line represents a linear sweep voltammogram of the Co oxide-modified electrode at a scan rate of 0.5 mV s⁻¹ in 0.05 M aqueous phosphate buffer solution at pH 7.0.

Figure 8 Current-time curves during electrolysis in various electrolyte aqueous solutions at pH 7.0 under the potentiostatic conditions of 1.3 V *vs.* Ag/AgCl. The working electrode was the Co oxide-modified electrode deposited at 10 °C.

Figure 9 Current-time curves during electrolysis in 0.05 M aqueous phosphate buffer solution at pH

7.0 using a Co oxide-modified electrode treated at 450 °C under the potentiostatic conditions of 1.3 V vs. Ag/AgCl. The Co oxide-modified electrode was prepared at 10 °C. Current-time curve during electrolysis for as-prepared Co oxide-modified electrode was taken from Fig. 8.

Figure 10 Surface AFM images of (a) as-prepared and (b) 450 °C heated Co oxide-modified electrodes. The Co oxide-modified electrode was deposited at 10 °C.

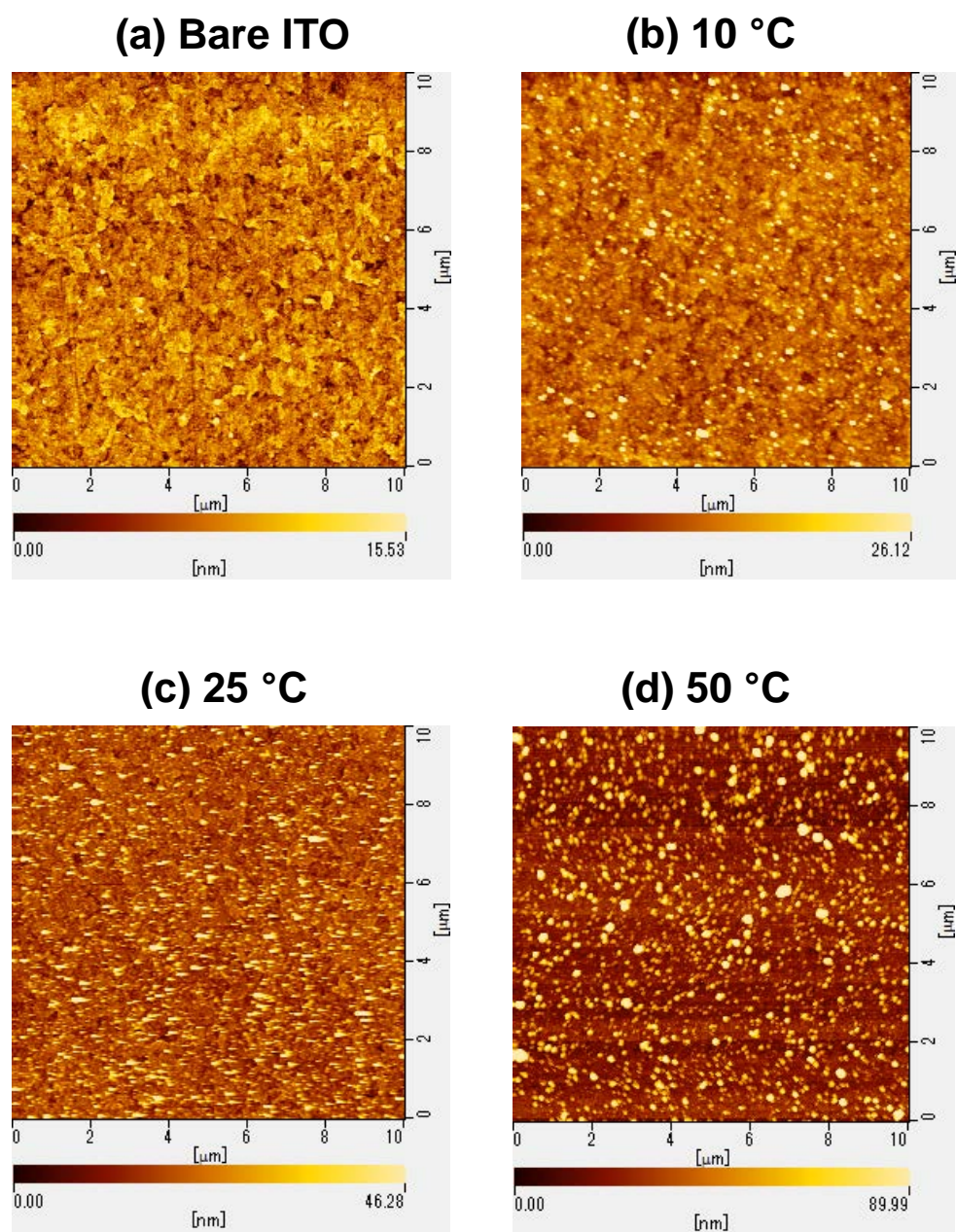


Figure 1

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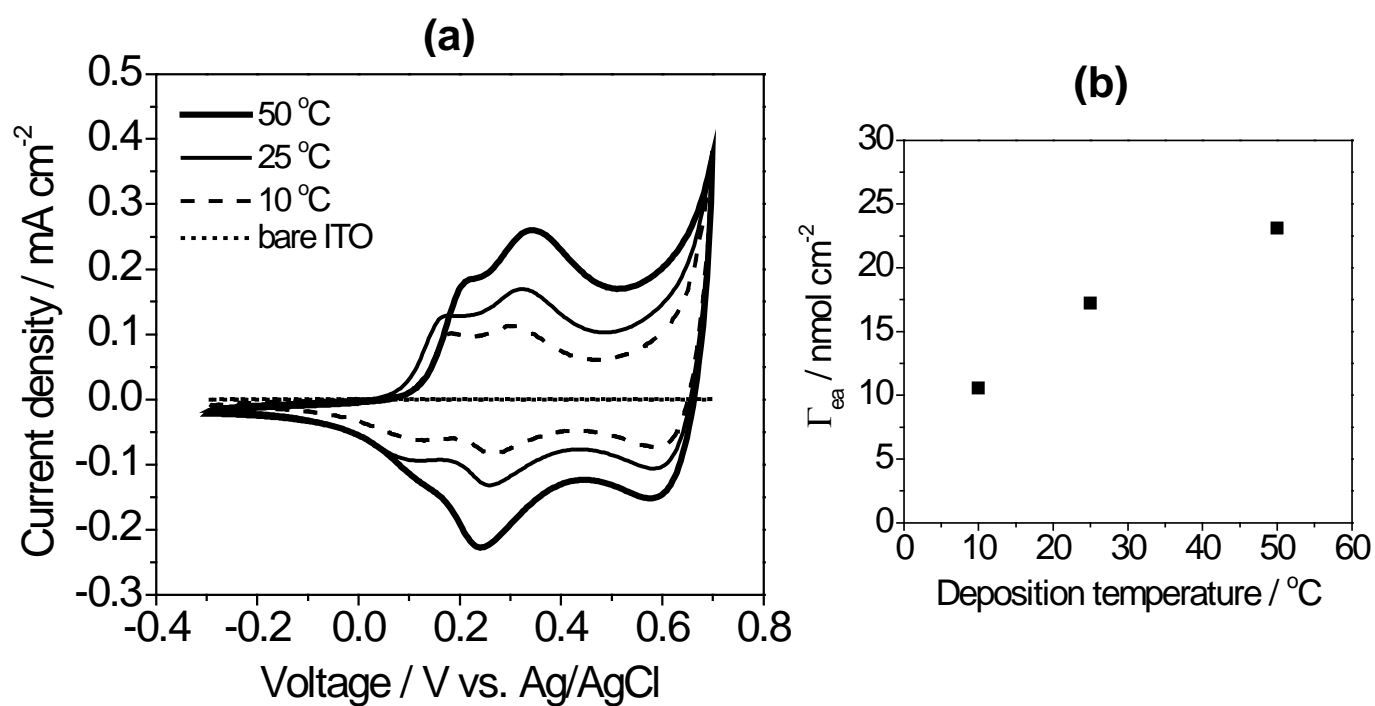


Figure 2

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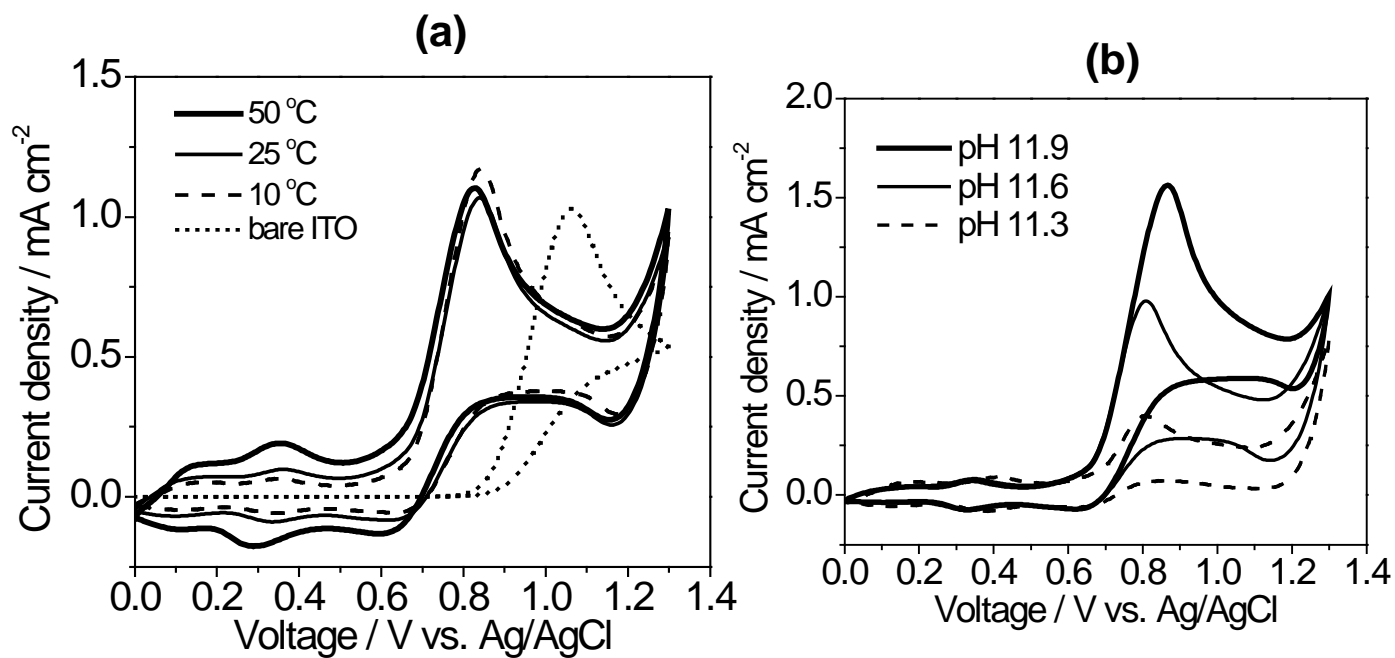


Figure 3

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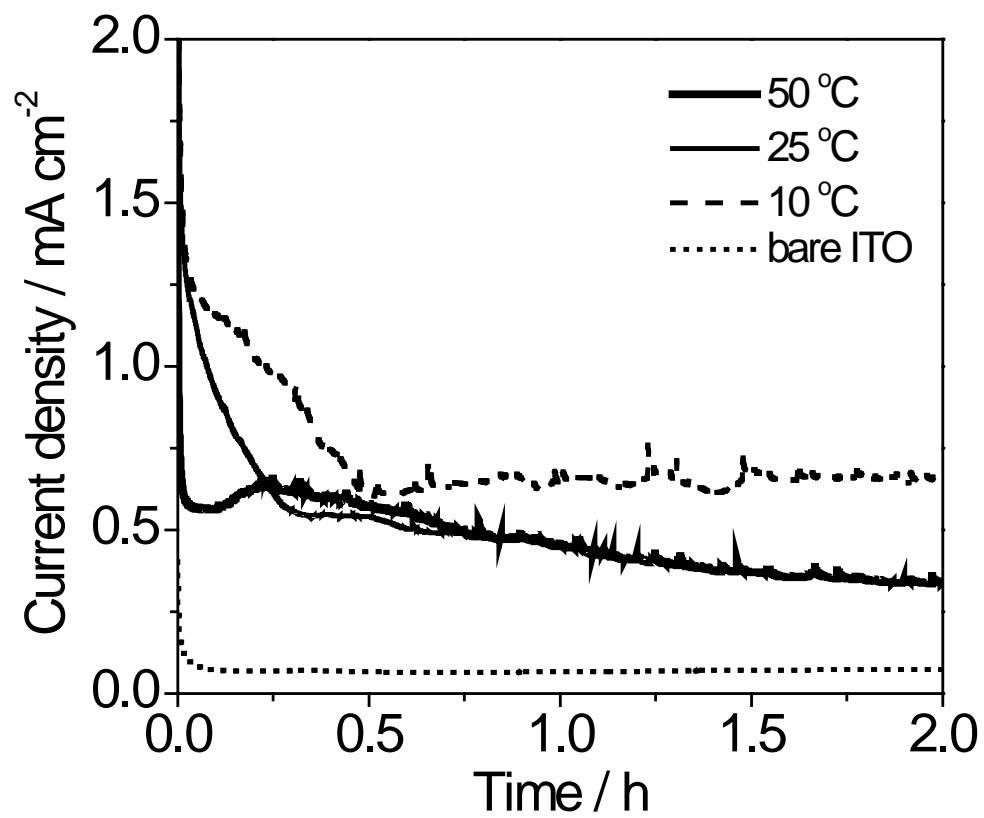


Figure 4

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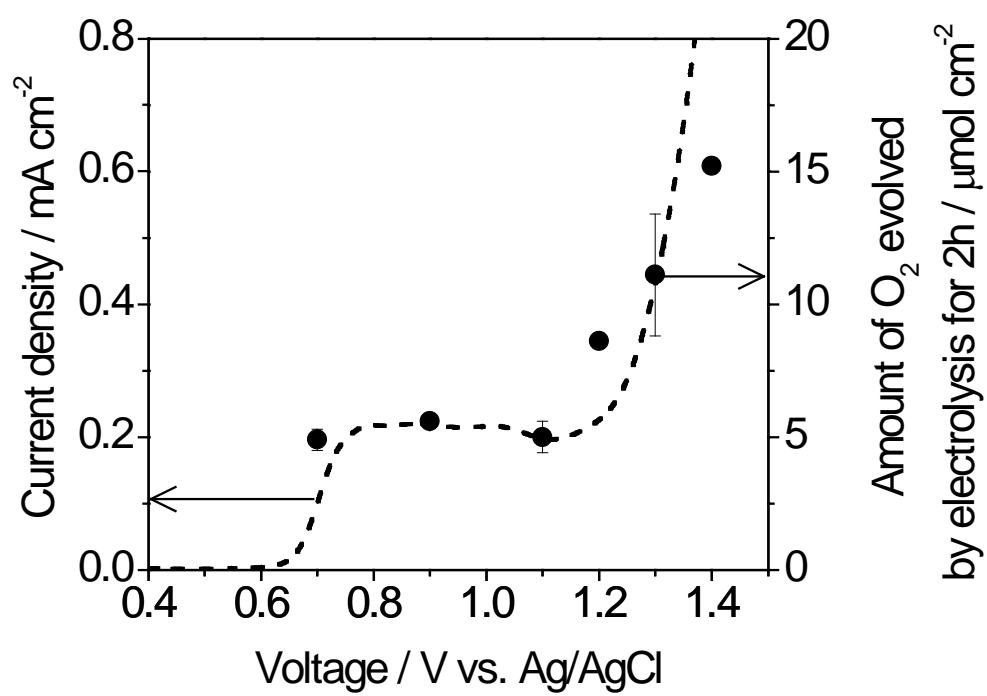


Figure 5

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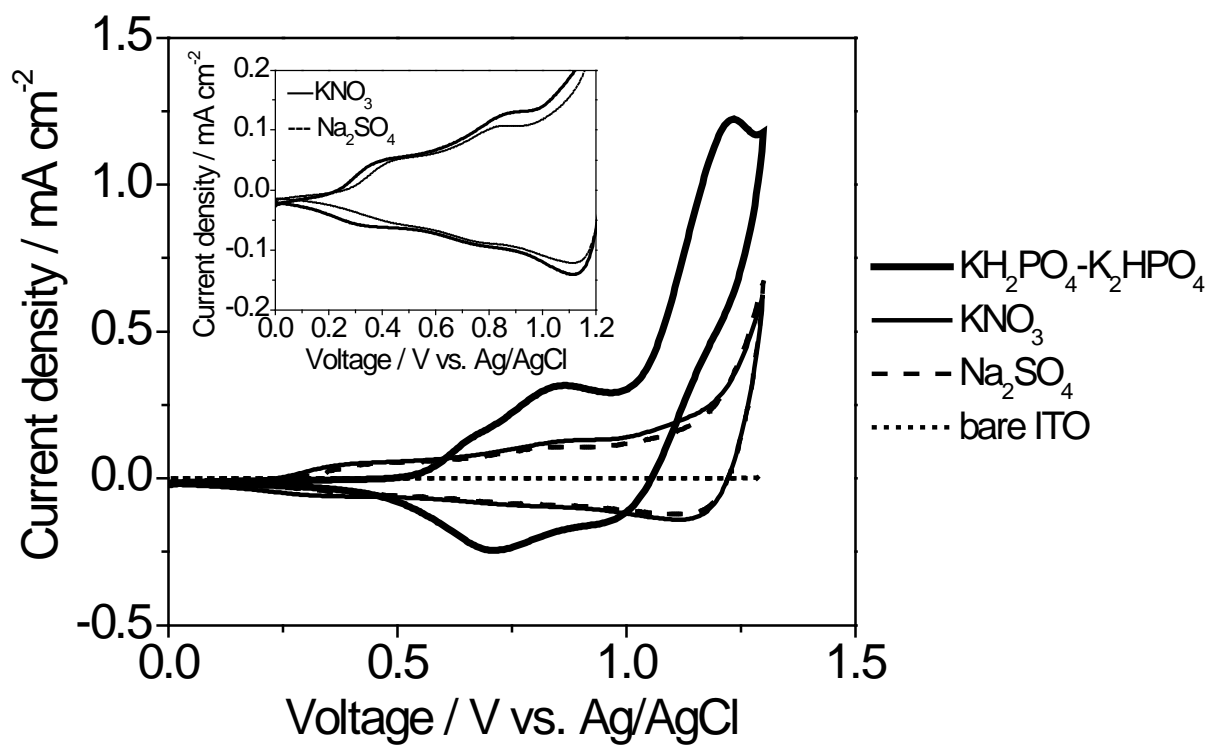


Figure 6

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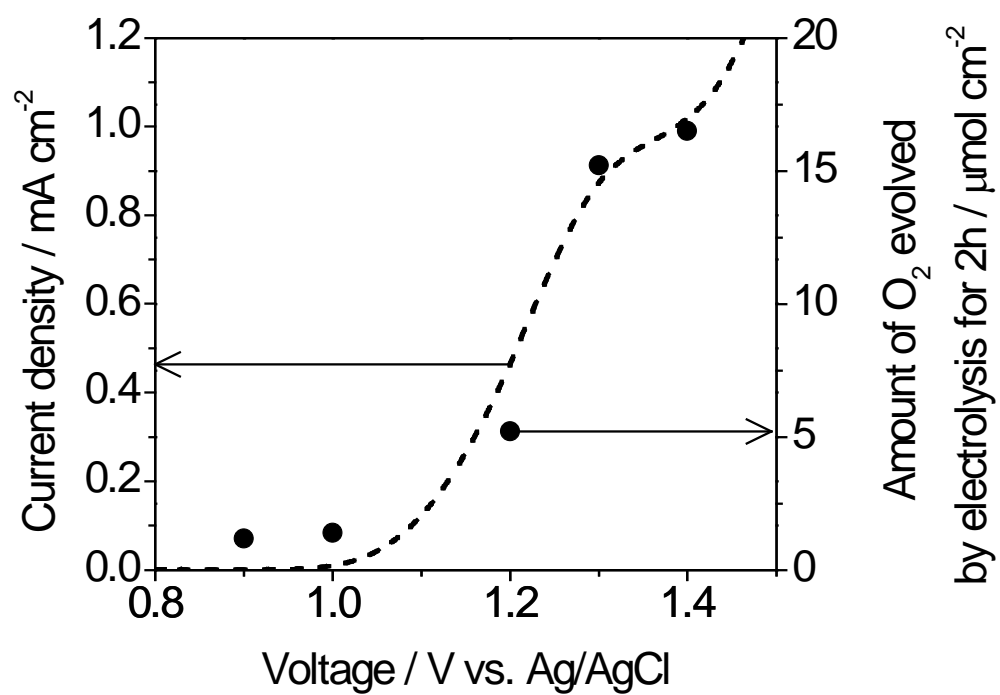


Figure 7

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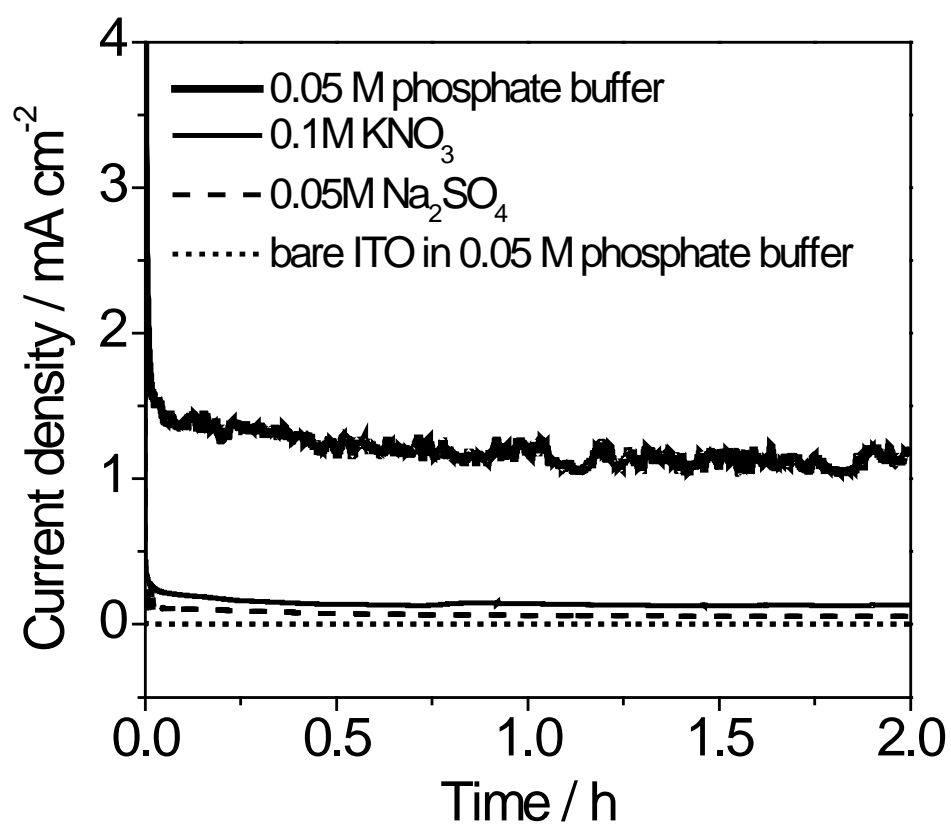


Figure 8

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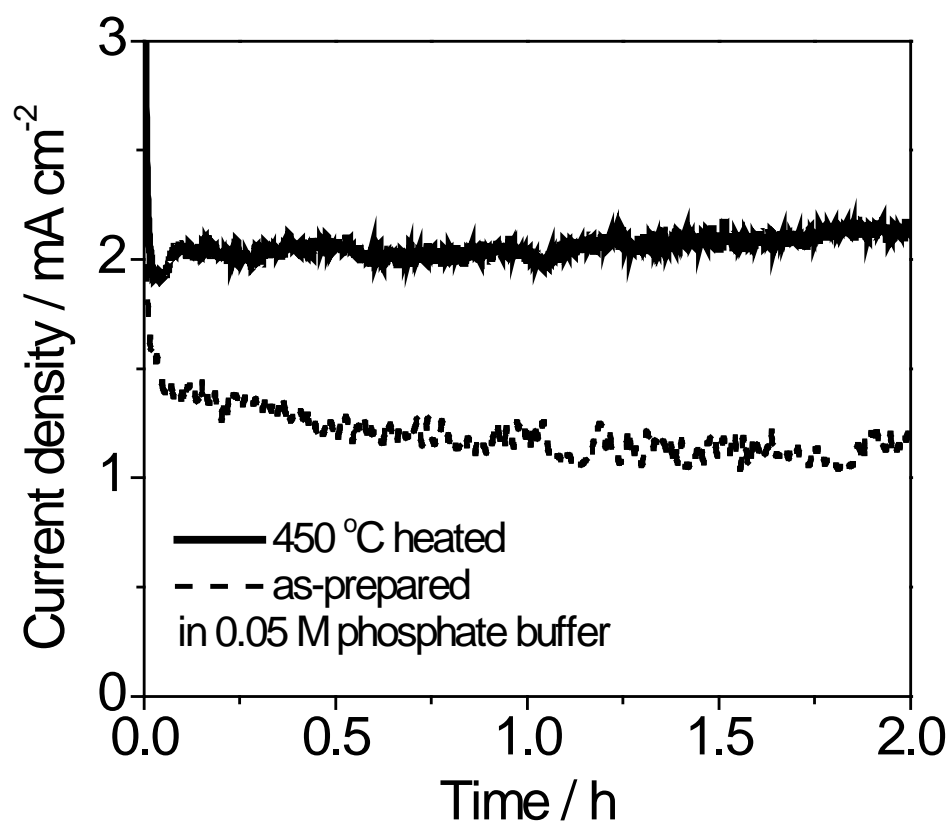


Figure 9

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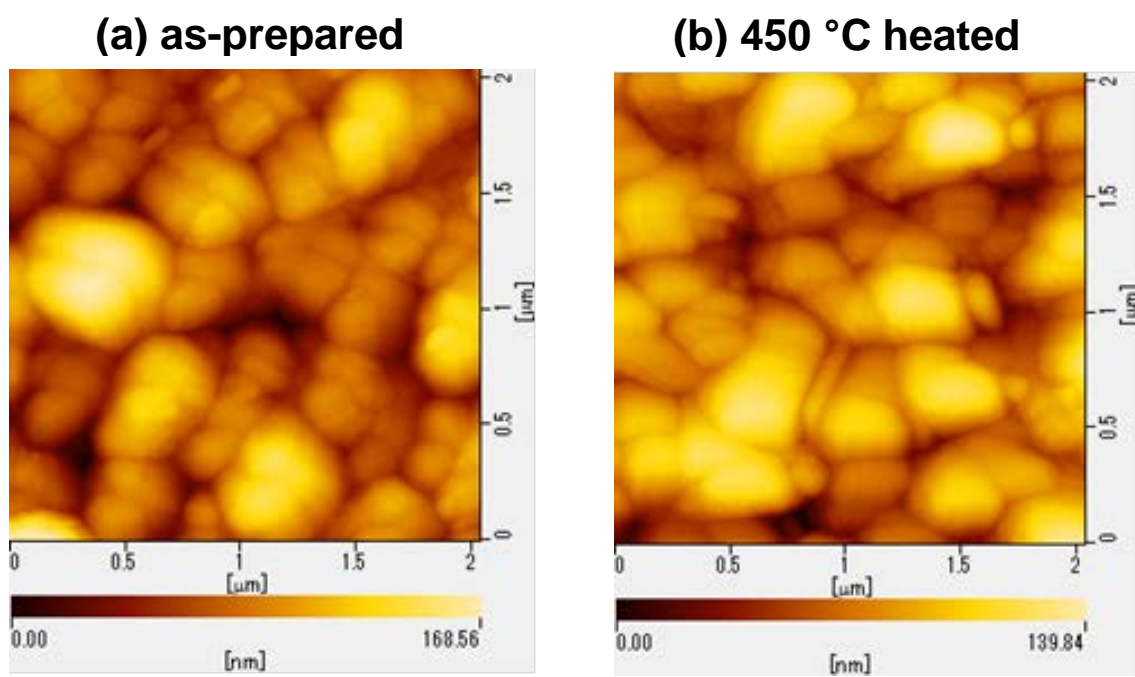


Figure 10

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