



Chemical bath deposition of IrO₂ films on ITO substrate

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Abstract

A chemical bath is shown to deposit an IrO₂ film on an ITO substrate. The chemical bath is prepared by mixing an Ir precursor (Na₃IrCl₆ · xH₂O), an oxidizer (NaClO), a complexing agent (NaNO₂), and a complex agent/stabilizer (NaOH) in an aqueous solution at a molar ratio of 1:1.5:10:30. From the UV–vis absorption spectra, complexes such as [Ir(OH)₆]m³⁻, [Ir(NO₂)₄Cl₂]³⁻, and [Ir(NO₂)₃Cl₃]³⁻ are identified. These complexes are relatively stable, minimizing the undesirable homogeneous precipitation of IrO₂ nanoparticles in favor of the heterogeneous growth of the IrO₂ film on the ITO substrate. Diffraction patterns from the as-deposited IrO₂ film reveal an amorphous structure. In addition, profiles from X-ray absorption spectroscopy and X-ray photoelectron spectroscopy indicate that the oxidation state of the Ir in the as-deposited IrO₂ film is +4. Thermogravimetric analysis confirms the inclusion of 10 wt% hydrated water in the as-deposited IrO₂ film. Scanning electron microscope images reveal a continuous solid film with a smooth surface. The amorphous IrO₂ film becomes rutile IrO₂ phase after a mild heat treatment in air.

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1. Introduction

The synthesis of iridium oxides has received considerable attention because iridium oxide has many unique properties that make it an ideal material for applications in electrochromism [1,2], bio-sensing [3–8], and water electrolysis [9–14]. To date, methods including thermal decomposition [15–17], sputtering deposition [13,18–20], pulsed laser deposition [21], and electrodeposition [6–9,11,22,23] have been explored for the fabrication of desirable nanoscale iridium oxide structures, such as thin films and nanoparticles. Thermal decomposition and sputtering deposition involve complex instrumentation, including heating and vacuum setups. Electrodeposition involves the use of suitable complexing agents in the plating bath to stabilize the iridium precursors (Ir³⁺ and Ir⁴⁺), which are known

to undergo spontaneous redox reactions triggered by photons [24]. In addition, electroplating techniques require a conductive substrate to serve as the working electrode, preventing the deposition of iridium oxide films on insulators.

An alternative solution for the synthesis is chemical bath deposition, in which the iridium precursors undergo oxidation reactions initiated by selectively incorporated oxidizers. This approach does not require externally imposed current/voltage and allows semiconducting materials to be used as the substrates for film growth [25–28]. So far, several studies have reported the formation of iridium oxide nanoparticles and investigated their electrocatalytic properties for oxygen evolution reactions in water splitting experiments [9–11,13,14,22,29–31]. However, these studies failed to describe the formation mechanisms of the iridium oxide and instead focused on material characterizations and performance evaluations. On the other hand, iridium oxide is a biocompatible electrode material which have been investigated to replace platinum to enhance the efficiency [32–34]. However, the preparation of iridium oxide traditionally uses

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sputtering process and consumes unnecessary noble target [6,7]. In addition, aspect ratio of the substrate is limited for the sputtering process. Therefore, chemical bath deposition does not require applying voltage/current or conducting substrates, so iridium oxide film can be coated on various materials, such as Si, SiO₂, and ITO, under ambient environments. Moreover, chemical bath deposition is a relatively cost efficient process because there is no extra precursor consumed, and it has better capability to coat iridium oxide onto targeting substrate. In order to better use, it is recognized that the surface composition, structure, and morphology play critical roles in determining the resulting properties. Hence, it is necessary to better understand and have control over the fabrication process to synthesize iridium oxides with desirable properties.

In the chemical bath used to form iridium oxides, the addition of complexing agents is necessary to inhibit unwanted redox reactions among the iridium precursors. Among the explored complexing agents, the hydroxide ions are often used to facilitate the synthesis of iridium oxide nanoparticles by stabilizing the iridium ions in the form of [Ir(OH)₆]²⁻; they also aid in hydrolysis and acid-catalyzed condensation, as well as precipitation reactions [12,14,23,30,35,36]. This process provides a facile route to prepare nanoparticulate iridium oxides but is ineffective for the deposition of iridium oxide thin films. Therefore, in addition to hydroxide ions, it is necessary to identify additional complexing agents to strengthen the stability of the complexed iridium ions and thus extend the lifetime of the plating bath, allowing heterogeneous precipitation to occur selectively on the intended substrates.

In this study, we demonstrate a formulation for the deposition of iridium oxide films (IrO₂) on an indium tin oxide (ITO) substrate *via* a chemical bath deposition route in which IrCl₆³⁻ is used as the Ir precursor, hydroxide ions (OH⁻) are used as the stabilizer and complexing agent, and nitrite ions (NO₂⁻) and hypochlorite ions (ClO⁻) are employed as the complexing agent and the oxidizer, respectively. The reaction steps responsible for IrO₂ formation are explored, and the material characterizations of the resulting thin films are discussed.

2. Experimental

2.1. Preparation of chemical bath

A glass slide coated with ITO (Aldrich; 8–12 Ω/sq) over an area of 2.5 × 2.5 cm² was utilized as the substrate for the chemical bath deposition. The thickness of the ITO coating was 120–160 nm. Prior to the deposition, the ITO substrate was rinsed with deionized water and acetone to remove any debris and contaminants. The deposition bath contained 0.0474 g (1 × 10⁻⁴ mol) Na₃IrCl₆ · xH₂O (Aldrich), 5.5674 g (1.49 × 10⁻⁴ mol) NaClO (SHOWA), 0.12 g (3 × 10⁻³ mol) NaOH (Mallinckrodt), and 0.069 g (1 × 10⁻³ mol) NaNO₂ (SHOWA). The Na₃IrCl₆ · xH₂O and NaClO were utilized as the precursor and oxidizer, respectively. The NaNO₂ was used as the complexing agent for the Ir precursor. The NaOH was used both as the complexing agent for the Ir precursor and the stabilizing agent for NaClO. A schematic of the preparation of

the chemical bath and the deposition process is depicted in Fig. 1. First, Na₃IrCl₆ · xH₂O was dissolved in deionized water, forming a pale yellow solution. Another transparent mixture was prepared by separately dissolving NaNO₂, NaOH, and NaClO in deionized water, and then these three solutions were mixed together. Once the Ir precursor solution was added to the transparent mixture, the resulting solution turned light yellow and was kept at 25 °C for 10 min. Subsequently, the light yellow solution was placed in a water bath at 70 °C for another 10 min, allowing the complexed Ir precursors to react with the oxidizer to form a dark blue solution. At this stage, the solution was ready for deposition, and the ITO substrate was immersed for 3 h to allow the growth of IrO₂.

2.2. Materials characterization

A UV–vis spectrometer (JASCO V-670) was used to record the absorption spectra of the deposition bath at 70 °C. A high-resolution X-ray diffractometer (XRD; Bruker D8 Discover) with a Cu Kα radiation source of 1.54 Å was employed to identify the phase and crystallinity of the IrO₂. Thermogravimetric analysis (TGA) was employed to determine the hydration

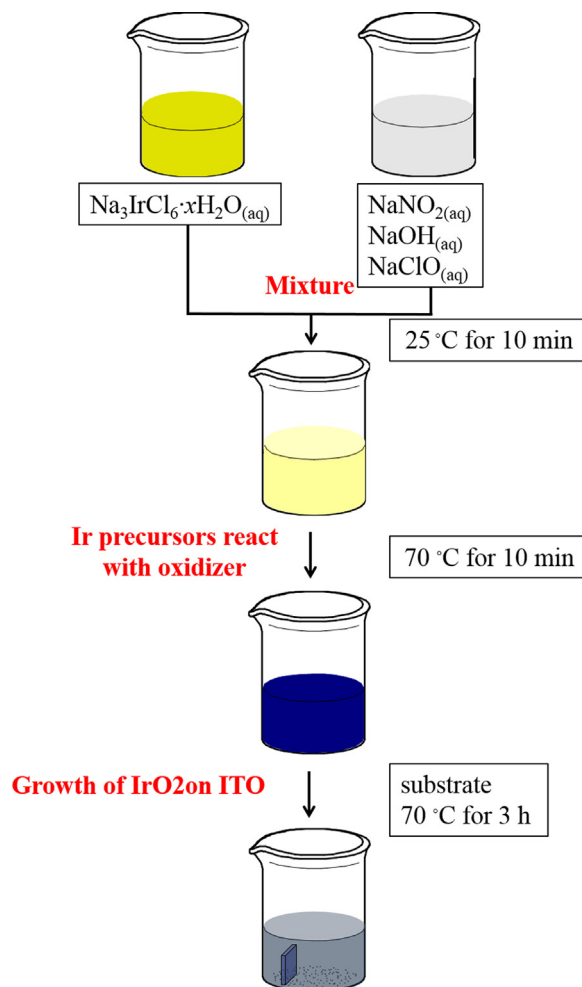


Fig. 1. An experimental flowchart of the processing steps for the IrO₂ deposition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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