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# Ultrafine Iridium Oxide Nanorods Synthesized by Molten Salt Method toward Electrocatalytic Oxygen and Hydrogen Evolution Reactions

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ABSTRACT

Ultrafine iridium oxide nanorods ($IrO_2$ NRs) were successfully synthesized using a molten salt method at 650 °C. The structural and morphological characterizations of these $IrO_2$ NRs were carried out by powder X-ray diffraction, Raman spectroscopy and electron microscopic techniques. Compared to commercial $IrO_2$ nanoparticles ($IrO_2$ NPs) and previous reports, these $IrO_2$ NRs show enhanced electrocatalytic activity to oxygen and hydrogen evolution reactions by passing either $N_2$ or $O_2$ gas in a 0.5 M KOH electrolyte before electrochemical measurements, including cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy. Specifically, the current densities from the as-synthesized $IrO_2$ NRs and commercial $IrO_2$ NPs were measured in 0.5 M KOH electrolyte to be 70 and 58 (OER, deaerated, at 0.6 V versus Ag/AgCl), 71 and 61 (OER, $O_2$, from −0.10 to 1.0 V versus Ag/AgCl at 50 mV/s), and 25 and 14 (HER, deaerated, at −1.4 V versus Ag/AgCl) $mA/cm^2$, respectively. These results are comparable with, and in most cases, higher than reported data in the literature. Therefore, the current study reports not only a novel synthetic process for $IrO_2$ but also a high efficient $IrO_2$ nanostructure, and it is expected that these $IrO_2$ NRs can serve as a benchmark in the development of active OER and HER (photo)electrocatalysts for various applications.

## 1. Introduction

The storage of renewable energy using hydrogen “fuel” has been viewed as a viable mechanism by electrolysis of water into oxygen and hydrogen fuels, but is hampered by the slow kinetics of the oxygen evolution reaction (OER). Hence there is a broad effort to improve performance of currently used materials and develop new materials. Iridium oxide ($IrO_2$) is an effective stable electro-catalyst which can lower the over-potential and keep a remarkable current to improve the efficiency of fuel generation technologies [1,2]. Nanostructured $IrO_2$ materials have been highlighted as the most promising electrode materials to enhance the electrocatalytic activity in both OER and hydrogen evolution reaction (HER) from the photo-electrochemical water-splitting and electrolysis [3,4,5,6,7,8]. Nanocrystalline $IrO_2$ and $RuO_2$ are recognized to be the best electrocatalysts for HER and OER in both acidic and alkaline media even though a growing body of OER and HER catalysts containing abundant, inexpensive transition metals and their oxides have recently appeared in the literature [9,10]. The continuous use of relatively expensive materials by industry is because the economics of electrolytic hydrogen production are governed mainly by catalytic performance rather than the catalyst cost and earth-abundant materials are typical not as stable [11]. Recently, Stoerzinger et al. have reported the surface orientated oxygen evolution activities of $IrO_2$ and $RuO_2$ in $O_2$-saturated 0.1 M KOH electrolyte at 1.53 V versus reversible hydrogen electrode [12]. The potentials range of $IrO_2$ electrocatalysts for OER were reported from 0.77 V to 1.5 V using acidic and alkaline solutions as the electrolytes [7,10,13,14,15,16,17,18,19]. The lowest potential of $IrO_2$ nanostructures was reported of 0.77 V for the OER in 0.1 M phosphate buffer solution using ITO electrode [13].

$IrO_2$ nanostructures have also been used widely as the electrocatalysts for the OER in proton exchange membrane (PEM) water electrolysis [15,16,20], solid polymer electrolyte (SPE) electrolyzer [13,17], photocatalytic and electrolysis of water oxidation, etc [3,6,8,13]. $IrO_2$ nanostructures were also used as the electrocatalysts in the oxygen reduction [1], oxidation of carbon mono-oxide, methanol and ethanol, etc [21,22]. Apart from the electrocatalysis, $IrO_2$ nanostructures were also used in several other applications including sensing [23], field emission [24,25], Li-air battery [26], electrical properties, etc [27].

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$IrO_2$ nanostructured materials were mostly synthesized by metal organic chemical vapor deposition (MOCVD) method [23,28,29,30,31,32,33,34,25]. A variety of $IrO_2$ nanostructures have also been produced by various other techniques, including vapor phase transport process [35], electrochemical synthesis [13], arc vaporization [36], hydrothermal [4], reactive radio frequency magnetron sputtering (RFMS) [37], sol–gel [38,39], wetness method [9], Adams fusion method [15,16], sulfite complex route [14], thermal decomposition of precursor ($H_2IrCl_6$) [17], oleylamine-mediated synthesis, etc [10]. With a closer look, it can be found that many of these methods employ expensive, complex, unstable and not-environmentally-friendly iridium-containing precursors followed with tedious synthetic procedure in complicated experimental setups. Molten salt synthesis process is the cost effective, stable and eco-friendly method compared to above reported methods. This method has also been employed earlier as a simple and facile approach in the synthesis of various nanostructured materials [40,41,42]. Herein, we report the successful synthesis of $IrO_2$ nanorods with an average diameter of ~15 nm and length of ~200 nm for the first time using iridium tetrachloride as precursor in a molten salt of sodium chloride and potassium chloride mixture at 650 °C for 12 h in ambient air atmosphere. The structural and morphological characterizations of $IrO_2$ NRs were investigated by powder X-ray diffraction (PXRD), Raman spectroscopy, energy dispersive X-ray studies, single point BET surface area measurements and electron microscopic studies. Note that an effective electrocatalyst can lower the over-potential to sustain the current and, therefore, to improve the efficiency of an electrocatalyst toward the gas evolution reactions due to loss of minimum energy in the electrochemical reactions. Electrocatalytic studies of the $IrO_2$ NRs toward OER and HER have been investigated by cyclic voltammetry (CV) and chronoamperometry (CA) in alkaline 0.5 M KOH aqueous electrolyte versus Ag/AgCl electrode, and obtained results were compared to commercial $IrO_2$ NPs and previously reported work.

## 2. Experimental

### 2.1. Materials and method

The following reagents were used in the synthesis of the $IrO_2$ NRs by the molten salt process: $IrCl_4$ (Alfa Aesar, 99.95%), NaCl (Alfa Aesar, 99.0%), and KCl (Sigma Aldrich, 99.0%). The precursors were taken with the molar ratio of 1:30:30 of $IrCl_4$:NaCl:KCl and ground together in an agate mortar pestle for 20 minutes. The resulting mixture was transferred to a covered rectangular crucible and kept at 650 °C for 12 h in a programmable high temperature furnace with the heating and cooling rate of 5 °C/minute in air. The resulting products were washed with de-ionized water several times and then dried at 60 °C for 6 h in oven. Commercial $IrO_2$ nanoparticles (NPs) from Sigma Aldrich (99.9%) were used to compare the electrocatalytic activity with the as-synthesized $IrO_2$ NRs.

### 2.2. Characterizations

The resulting fine black colored powder of the $IrO_2$ NRs was characterized initially by PXRD on a Rigaku MiniFlex X-ray diffractometer using Ni-filtered Cu-Kα radiation. Diffraction patterns were recorded with a step size and scan speed of 0.01° and 1 s, respectively, on an aluminum sample holder. Raman scattering data was recorded by employing the back-scattering geometries on a Bruker SENTERRA RAMAN microscope with an objective of 20X optical microscope. The excitation line (785 nm) of an Ar+ laser beam was focused to a spot size of 5 μm with a laser power of 25 mW. The used spectral resolution range was 3–5 $cm^{-1}$ with the integration time of 100 s. Field emission SEM study was carried out with a ZEISS SIGMA VP electron microscope operated at 5 kV. Transmission electron microscopy (TEM), high resolution TEM (HRTEM), and selected area electron diffraction (SAED) analyses were carried out with a Hitachi H-9500 electron microscope operated at 300 kV. The samples for TEM studies were prepared by dispersing the $IrO_2$ NRs in ethanol via utrasonic process for 5 minutes, and a drop of the formed suspension was put onto a carbon coated copper grid, and then dried in air. Surface area analysis was performed on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer with nitrogen at cryogenic temperature (77.3 K).

### 2.3. Preparation of electrode materials and electrochemical measurements

The working electrode was modified with the as-synthesized $IrO_2$ NRs for the electrochemical studies toward OER and HER. The $IrO_2$ nanostructures modified electrodes were prepared by mixing the nanopowder, carbon black and PVDF. The powder of $IrO_2$ NRs was ground with carbon black and PVDF in the weight fraction of 75:15:10, with a small amount of ethanol and then pasted on the glassy carbon electrode. The prepared electrode materials were then dried overnight at 65 °C in vacuum oven. The electrochemical

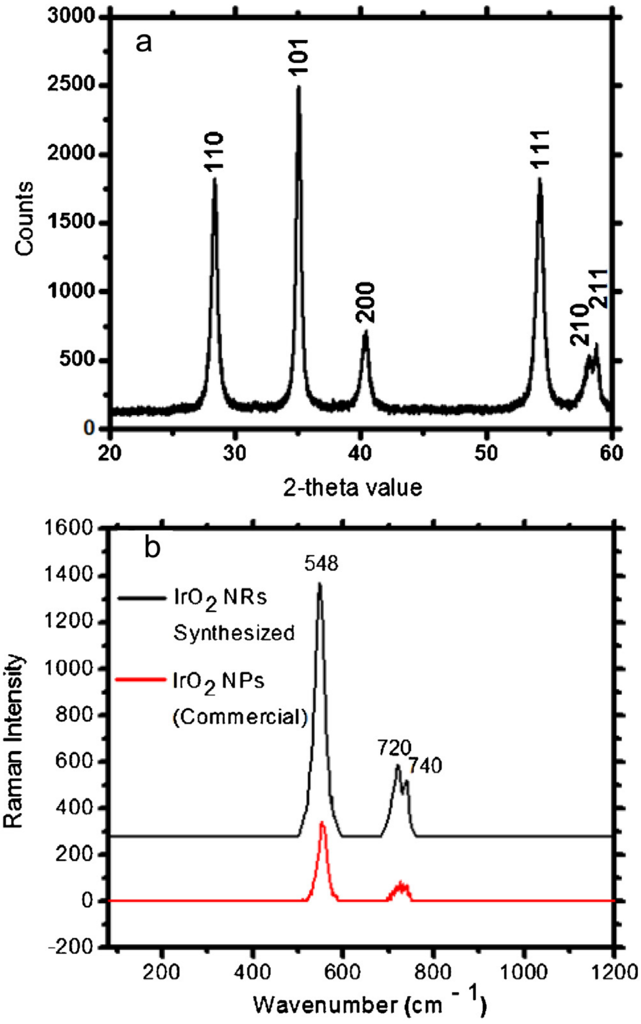

**Fig. 1.** (a) Powder x-ray diffraction pattern of the $IrO_2$ NRs synthesized by the molten salt process at 650 °C for 12 h. (b) Raman spectra of the $IrO_2$ NRs and commercial $IrO_2$ NPs.