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Short Communication

Oxidized iridium nanodendrites as catalysts for oxygen evolution reactions

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ABSTRACT

Iridium nanodendrites were synthesized using tetradecyltrimethyl ammonium bromide (TTAB) as an organic capping agent, and the electrocatalytic activity toward oxygen evolution reaction (OER) was evaluated. X-ray photoelectron spectroscopy revealed that an anodically grown iridium oxide film was created on the Ir dendrite through a repeated potential sweep between 0.04 and 1.54 V vs. SHE. The highly branched structure of the Ir dendrites with a particle size of ~10 nm provides an increased active facet area that is available for OER in comparison to a commercial Ir catalyst, resulting in enhanced activity toward OER.

1. Introduction

Hydrogen is expected to be an important part of the future of renewable energy because it is a recyclable, nonpolluting energy carrier [1,2]. Although at present hydrogen is predominately generated during the processing of fossil fuels, much effort has been devoted to producing hydrogen from water electrolysis driven by renewable energy sources; water electrolysis is technologically simple, environmentally clean, and it generates hydrogen in high purity. Water electrolysis using a proton exchange membrane (PEM) is an attractive system that possesses certain advantages over traditional alkaline processes in terms of efficiency and specific production capacity [3,4]. However, one of the major problems for PEM water electrolysis is the high overpotential associated with an oxygen evolution reaction (OER) that occurs at the anode. Both the acidic environment and the high potential during water electrolysis limit the choice of anode material to noble metals, such as iridium or iridium-based mixed oxides, which display high activities toward OER [5–7]. Nanosized noble metal catalysts were synthesized by several preparation methods including the Adams fusion [8], sol-gel method [9] and a sulfite-complex route [10] to achieve a large surface area because the activity toward oxygen evolution reaction decreases with increasing particle size [11].

In recent years, due to the high costs and limited availability of noble metals, intensive research efforts have been focused on controlling the shape of noble metal nanoparticles to improve catalytic activity. Nanoparticle shapes can be altered to include distinct facets and atomic arrangements. Controlling the shape of catalytic nanoparticles can significantly influence catalytic properties, such as activity and selectivity [12,13]. Somorjai et al. synthesized rhodium nanocubes using a seedless polyol method and measured the catalytic activity of these particles toward CO oxidation [14]. Pt nanocubes were synthesized using PVP controllers and Fe^{3+} ions in a polyol process. These nanocubes displayed a dominant {100} facet and showed a lower onset potential as well as higher activity toward methanol and ethanol electro-oxidation than did polycrystalline Pt catalysts [15]. Recently, tetrahexahedral Pt nanoparticles with 24 high-index facets were prepared in high yield through the electrochemical treatment of Pt nanospheres. These high energy surfaces exhibited enhanced catalytic activity with respect to electro-oxidation of formic acid and ethanol [16]. Pt–Pd bimetallic nanodendrites showed higher activity toward an oxygen reduction reaction (ORR) than did conventional Pt/C catalysts due to the increased active facet area available to ORR [17].

The success achieved in enhancing catalytic activity through controlling nanoparticle morphology, reviewed briefly above, suggests that the shape control of iridium would improve the material's activity toward OER; however, little has been reported with respect to shape controlled iridium. In the present study, iridium shape was controlled to produce dendrites using tetradecyltrimethyl ammonium bromide (TTAB) as an organic capping agent. The activity of OER for the prepared Ir dendrites was evaluated and compared to commercial Ir catalysts using a conventional three electrode system.

2. Experimental

$H_2IrCl_6 \cdot xH_2O$ (Alfa Aesar, 99.9%) and TTAB (Aldrich, 99%) were mixed with 10 mL of deionized water at room temperature. The molar ratio of iridium salt to TTAB was 1:100. The mixture was heated at 50 °C for 20 min until the solution became a clear dispersion.

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Subsequently, ice-cold sodium borohydride was added to the solution, and it was maintained at 50 °C for 6 h. The resulting solution was centrifuged at 14000 rpm for 10 min, and the sediment was collected. To prepare the electrode, the catalyst powder was mixed with a Nafion (5 wt.%), isopropyl alcohol and water (Nafion: 0.05 mL, IPA: 1.5 mL, water: 0.5 mL) in an ultrasonic bath. The resulting suspension (6 μL) was dropped onto the gold disk of a rotating disk electrode (RDE, Pine Instrument, 0.196 cm^2) using a micro pipette and was dried in a nitrogen chamber. The total loading of Ir catalyst on the RDE was fixed at 50.5 μg cm^{-2}.

For electrochemical characterization, a conventional three electrode system involving 0.5 M H_2SO_4 saturated with nitrogen was used. Working and counter electrodes included an RDE and a platinum wire, respectively. A standard $Hg/HgSO_4$ electrode served as a reference electrode. All of the potentials reported herein, however, are with respect to a standard hydrogen electrode (SHE). The activity of the OER was measured using a three-electrode cell at a sweep rate of 5 mV s^{-1}. Prior to OER measurement, TTAB on the surface of Ir was removed using a potential sweep between 0.04 and 1.54 V vs. SHE at a scan rate of 50 mV s^{-1} three times [18]. Cyclic voltammograms was recorded using the three electrode system in a nitrogen-saturated 0.5 M H_2SO_4 solution at 5 mV s^{-1} between 0.04 V and 1.24 V vs. SHE. The morphology of the synthesized Ir dendrites was examined by high-resolution transmission electron microscopy (HR-TEM) using a JEM-30100 microscope. X-ray diffraction (XRD) was carried out to characterize the crystalline structure. X-ray photoelectron spectroscopy (XPS, Sigma probe UK) was performed to analyze the surface composition of catalysts.

3. Results and discussion

HR-TEM images of iridium dendrites and a commercial iridium catalyst (Johnson Matthey Co. JM, 99.95% (metal basis), specific surface area: >30 m^2 g^{-1}) are shown in Fig. 1. The commercial Ir catalyst displayed extensive agglomerates of Ir particles. In contrast, the synthesized Ir dendrites were dendritic and had branches in various directions. The size of each iridium dendritic nanoparticle was on the order of 10 nm. Detailed examination of the iridium dendrites, as shown in Fig. 1d, revealed a connected atomic arrangement that rendered the entire nanostructure single-crystalline. Fourier transform (inset) of the atomic lattice showed a dotted pattern, indicating that it was indeed single-crystalline and not an agglomeration of small, distinct nanoparticles. Fig. 2 displays the XRD pattern of the prepared iridium dendrites. Four major peaks at 40.6, 47.3, 69.1, and 83.4° were assigned to diffractions from the {111}, {200}, {220}, and {311} planes of the face-centered cubic Ir metal (JCPDS Card No. 87-0715). No evidence of IrO_2 was observed in the XRD patterns.

The prepared Ir dendrites were used as electrocatalysts for OER. Fig. 3 shows typical polarization curves for the OER on the Ir dendrite using a rotating disk electrode in a nitrogen-saturated 0.5 M H_2SO_4 solution with a rotation rate of 1200 rpm to remove oxygen bubbles generated on the surface of electrode. For comparison, the curve for the commercial Ir catalyst was plotted under the same conditions. As shown in the inset of Fig. 3, since the OER does not change with the increase of the RDE rotating speed, the OER is not controlled by mass transfer in this system. As can be observed from the polarization curves, the increased anodic current was obtained with the iridium dendrites at all potentials in which the OER can be activated. The anodic current, measured at a potential of 1.6 V, was 5.5 times higher for the Ir dendrites. This result indicated that an OER could occur more easily for the Ir dendrite catalyst.

In Fig. 4, cyclic voltammograms (CV) are shown for the Ir dendrites and commercial Ir catalyst. When CV was performed for the fresh Ir dendrite catalyst between 0.04 and 0.64 V_{SHE} to avoid oxide formation, hydrogen adsorption and desorption peaks typical for noble metals were detected. However, after the three cycles of potential sweep up to 1.54 V_{SHE} for the pretreatment process to

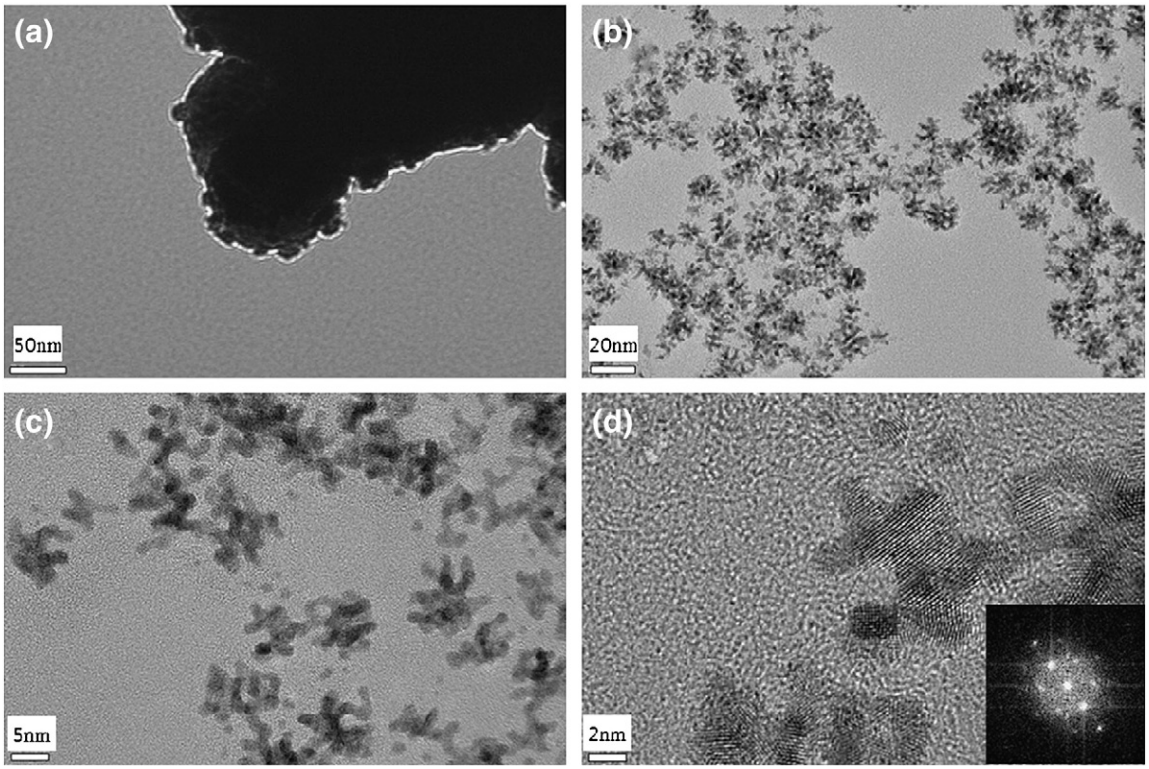

Fig. 1. HR-TEM images of (a) commercial iridium (Johnson Matthey) and (b–d) iridium dendritic nanoparticles at different magnifications. The inset image in (d) shows the corresponding Fourier transform pattern of the iridium nanodendrites.