Synthesis of iridium oxide nanosheets and its activity for oxygen evolution reaction

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Abstract: Iridium dioxide (IrO_2) nanosheets with thickness of less than 1 nm was prepared via exfoliation of layered iridic acid ($H_xIr_yO_z{\cdot}nH_2O$), which was prepared via proton exchange of layered potassium iridate ($K_xIr_yO_z{\cdot}nH_2O$). The mass activity for oxygen evolution reaction (OER) of IrO_2 nanosheets was 8 times higher compared to IrO_2 nanoparticles. The OER specific activity can be improved by down-sizing the lateral size of IrO_2 nanosheets.

Keywords: Metal oxide nanosheet, Oxygen evolution reaction, Edge effects.

1. Introduction

Two-dimensional nanomaterials are typically obtained via exfoliation of ion-exchangeable layered oxides and have been offered attractive properties. Rutile-type IrO_2 is iso-structural with RuO_2 and both share many of the electrochemical advantageous. IrO_2 is well known as an electrocatalyst with high resistance to corrosion at high potential and is used as an electrocatalyst for oxygen evolution reaction. Although RuO_2 is also active for OER, the stability of RuO_2 is not as high as IrO_2 at high potentials (>1.4 V vs. RHE), due to the oxidation to a soluble species in acidic environments. Therefore, IrO_2 is the favored electrocatalyst for OER.

In order to improve the OER activity of IrO_2, various nanomaterials with high specific surface area have been proposed (e.g. nanoparticles, nanotubes, and mesoporous materials). Nanosheets may potentially offer higher electrochemically active surface area and thus higher utilization for electrochemical reactions in comparison to typical nanostructured material. Here, we report the first successful synthesis of two-dimensional IrO_2 nanosheets with thickness of less than 1 nm, and the lateral size effect of IrO_2 nanosheet on OER activity was discussed[1].

2. Experimental

IrO_2 nanosheet was derived via exfoliation of layered $H_xIr_yO_z{\cdot}nH_2O$ through a process reported previously. Briefly, a mixture of K_2CO_3 and IrO_2 was pelletized and calcined under Ar flow. After washing with deionized water to remove water-soluble impurities, the product was treated with HCl for 3 days at 60°C. The acid-treated sample was reacted with an aqueous solution of tetrabutylamonium hydroxide for 7 days. The suspension was centrifuged to remove non-exfoliated material. The final colloidal contains IrO_2 nanosheets with a dark indigo color. The lateral size of IrO_2 nanosheet was reduced by ultrasonic treatment with a homogenizer. The working electrode was prepared by dropping 20 μL of IrO_2 nanosheet (100 mg mL^{-1}) on a glassy carbon electrode (6 mm in diameter). A thin layer of Nafion ionomer was cast on the electrode. All electrochemical measurements were conducted in 0.1 M $HClO_4$ (25^oC).

3. Results and discussion

The morphology of the sample after acid-treatment was characterized. Copious cracks in the platelets are observed after the acid treatment, suggesting an opening up of the framework and a reactive interlayer. A typical AFM image reveals individual nanosheets with lateral size ranging from a few hundred nanometers to a few micrometers (equivalent diameter (D_e) of 258 nm) and average thickness of 1.5±0.3 nm (Fig. 1).

The lateral size of as-prepared IrO_2 nanosheet decreased from 258 nm to 111 nm by ultrasonic treatment of 30 min.

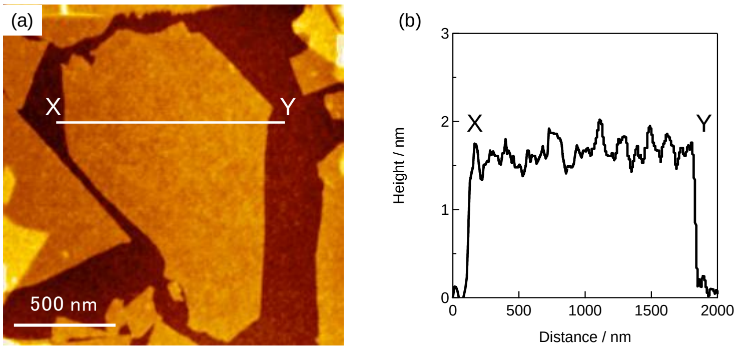

Figure 1. (a) Typical AFM image and (b) corresponding height profile of IrO_2 nanosheet.

The electrochemically active surface area obtained from the electric double layer capacitance (C_{dl}) for all nanosheets was similar. The overall specific capacitance (C_{all}), which was calculated by averaging the anodic and cathodic charges measured by cyclic voltammetry, was increased with decreasing the lateral size of IrO_2 nanosheets. The higher C_{all} of smaller-sized nanosheets was attributed to the larger the redox-related capacitance (C_{redox}).

The OER mass activity of IrO_2 nanosheets increased with decreasing the D_e. IrO_2ns(110nm) exhibited 2.5 times higher activity than IrO_2ns(260nm) and 8.4 times higher OER mass activity than nanoparticles. The increase in OER specific activity is discussed based on the increase in the edge/plane ratio (Fig. 2). The trend in the improvement factor for the edge/plane ratio corresponded well to that for the OER mass activity, suggesting that the edge sites of IrO_2 nanosheets act as active site for OER.

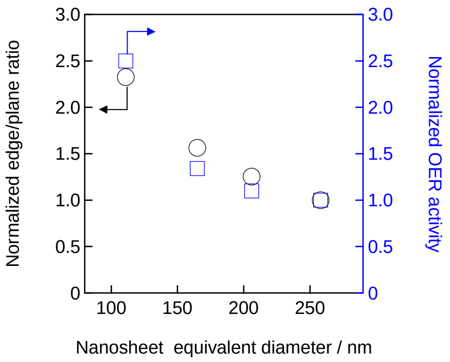

Figure 2. Normalized edge/plane ratio and normalized OER mass activity for IrO_2 nanosheets as a function of D_e.

4. Conclusions

IrO_2 nanosheets was successfully prepared via exfoliation of layered oxide. The OER mass activity of IrO_2 nanosheet can be enhanced by decreasing the lateral size of the IrO_2 nanosheets. The higher C_{all} of smaller-sized nanosheets was attributed to the higher C_{redox} on the metal oxide surface, since C_{dl} does not change by decreasing D_e. The enhanced OER specific activity with decreasing D_e is attributed to the edge effects of nanosheets.

References

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