

Structure of Pt/Ir/IrO₂tubes and Their electrocatalytic Properties in Oxidation of Small Organic Molecules

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A Pt-Ir-IrO₂NT structural electrocatalysts of high activity is synthesized using IrO₂ thin-wall nanotubes grown in CVD. The IrO₂ single-crystal wall constrains the Ir grains nucleated in lattice oxygen removal to a preferred direction so that the synthesized PtIr catalysts exhibit the structural characteristics of Ir(110) plane. The synthesis procedure involved reduction of IrO₂NT following electrodeposition of Pt. The Pt-Ir-IrO₂NT catalysts are approximately of 1100 nm in height and 80-100 nm in diameter, vertically aligned on a sapphire substrate. Their structural features and catalytic activities were studied using scanning electron microscopy, transmission electron microscopy, X-ray powder diffraction, and cyclic voltammetry toward CO_{ad} and methanol oxidation.

Lattice oxygen of IrO₂NT is removed under high-vacuum thermal annealing to facilitate nucleation of 3-5 nm Ir grains and subsequent PtIr synthesis. Interestingly, the apparent dimensions and orientation of IrO₂NT can be preserved via pore generation in the oxygen removal process. The tubular wall was transformed from a thin dense plate of IrO₂(110) single crystal into a porous plate consisting of connected Ir grains that exhibit lattice fringes of the Ir{110} spacing with preferential orientation of Ir[1 $\bar{1}$ 0] parallel to the IrO₂NT growth direction, shown in Fig. 1. The amount of Ir being reduced, the Ir grain size, and the size of deposited Pt strongly influence the surface area and the catalyst activity. The Pt-Ir-IrO₂NT catalyst reduced at 500°C exhibits a significantly higher activity than those of Pt-IrO₂NT and Pt-IrNT in methanol oxidation, also a higher current density than that of a Johnson-Matthey PtRu catalyst in the high potential region. The methanol oxidation voltammograms of Pt(2.9nm)-Ir(4.5nm)-IrO₂NT, Pt(3.2nm)-Ir(4.5nm)-IrO₂NT, Pt(5.1nm)-Ir(11.3nm)NT, Pt(5.5nm)-IrO₂NT, HiSPEC 6000 Pt:Ru=1:1 (Johnson-Matthey), Ir(11.3nm)NT, Ir(4.5nm)-IrO₂NT, IrO₂NT are illustrated in Fig. 2.

Details on the growth conditions of vertical IrO₂ nanotubes (IrO₂NT) can be found in our previous publications.¹

Reference

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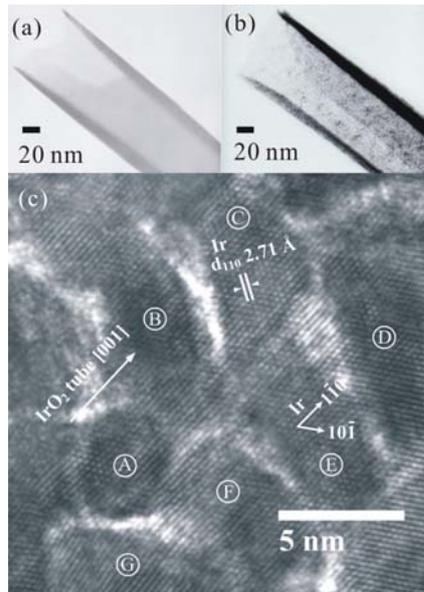


Fig. 1 Structural variations in the IrO₂ tube wall before and after the lattice oxygen removal. Two bright field TEM images of (a) an IrO₂ tube and (b) a 500°C-reduced tube, please note the wall fragmentation in (b). The atomic image of a 500°C-reduced tube wall in (c) was taken with a zone axis of Ir[$\bar{1}11$]. Note the same lattice fringe of various Ir grains except grain ③.

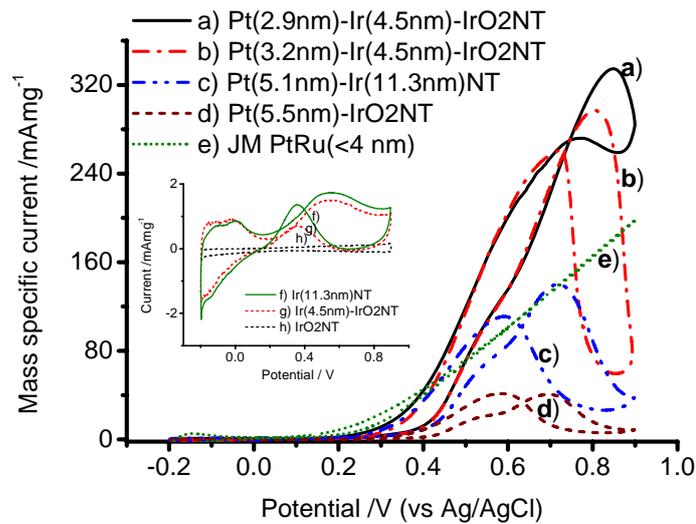


Fig. 2 Cyclic voltammograms of (a) Pt(2.9nm)-Ir(4.5nm)-IrO₂NT, (b) Pt(3.2nm)-Ir(4.5nm)-IrO₂NT, (c) Pt(5.1nm)-Ir(11.3nm)NT, (d) Pt(5.5nm)-IrO₂NT, (e) HiSPEC 6000 Pt:Ru=1:1 (Johnson-Matthey), (f) Ir(11.3nm)NT, (g) Ir(4.5nm)-IrO₂NT, (h) IrO₂NT, measured in a solution containing 2.5 M methanol and 0.5 M H₂SO₄ at 25°C and 10 mVs⁻¹.