Microstructure and morphology of thermochemically formed IrO$_2$ and Ir

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Over the past several years, the researchers and engineers focused on the synthesis of IrO$_2$ thin films or IrO$_2$ powders and on the investigation of their properties. IrO$_2$ thin films and powders are characterized with specific physical and chemical properties, which made them suitable for the application in advanced technologies, for example, as electrode materials for the production of components in advanced memory technologies. IrO$_2$ combines high chemical inertness and ohmic conductivity comparable to that of common metals. IrO$_2$-based resistors were made for application in piezoresistive sensors. IrO$_2$-Ta$_2$O$_5$ and IrO$_2$-RuO$_2$ coated electrodes have found application in electrochemistry. The physical and chemical properties of IrO$_2$ thin films and powders strongly depended on the route of their synthesis. In other words, controlling the route and parameters of the IrO$_2$ synthesis, it is possible to pronounce some physical or chemical property which is important for specific application of IrO$_2$. The present work focuses on the formation of IrO$_2$ powder by the thermal treatment of iridium(IV)-oxide dihydrate (IrO$_2$ \cdot 2H$_2$O) or iridium(III)-acetylacetonate (Ir(acac)$_3$).

The formation of IrO$_2$ and Ir by thermal decomposition of IrO$_2$ \cdot 2H$_2$O and Ir(acac)$_3$ in air ambient has been investigated by Raman Spectroscopy (RS), Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED).

Starting material, IrO$_2$ \cdot 2H$_2$O was amorphous, as found by XRD [1]. SAED pattern of that sample furthermore evidenced the presence of amorphous material (Fig. 1). Raman spectrum of IrO$_2$ \cdot 2H$_2$O showed two broad bands at 708 cm$^{-1}$ and 544 cm$^{-1}$. An additional broad band at 352 cm$^{-1}$ was interpreted in sense of poor crystallinity and/or presence of very fine particles that tend to periodic aggregation. The aggregation was also documented by TEM as shown in Fig. 1. Upon the heating of the IrO$_2$ \cdot 2H$_2$O at 600 °C the band at 352 cm$^{-1}$ disappeared. At 600 °C, nanosized IrO$_2$ particles with layered microstructure were formed (Fig. 2). The crystallites of IrO$_2$ had mainly the parallelepiped-like shape and sizes were about 30 nm.

Ir(acac)$_3$ decomposed in air at 200 °C, yielding Ir and traces of IrO$_2$. An increase of heating temperature leads to an increase in IrO$_2$ fraction. A gradual increase in crystallite size of Ir from 11(3) to 30(7) nm with change of temperature from 200 to 500 °C and increase crystallite size of IrO$_2$ from 12(4) to 20(5) nm with change of temperature from 350 to 550 °C were estimated by Scherrer method [1]. Raman bands of IrO$_2$ at 718 and 546 cm$^{-1}$ were observed (Fig. 3). These wave numbers are smaller than those of IrO$_2$ single crystal. The crystallite sizes of formed materials, revealed in high resolved TEM images, were about 10 nm. Heating temperature of 550 °C enhanced IrO$_2$ fraction and induced growth of crystallite sizes of both IrO$_2$ and Ir. At the same temperature thin Ir metal films were separately formed.

The results of present study showed that nanosize IrO$_2$ particles can be produced by thermal treatment of amorphous IrO$_2$ \cdot 2H$_2$O and Ir(acac)$_3$ in air.

Figure 1: TEM and SAED pattern of amorphous IrO$_2$·2H$_2$O particles.

Figure 2: Nanosize IrO$_2$ particle obtained by heating IrO$_2$·2H$_2$O at 600 °C.

Figure 3: Room temperature Raman spectra of IrO$_2$, prepared by heating Ir(acac)$_3$. Temperature of IrO$_2$ preparation are denoted above spectra.