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 piesoresistive sensors. IrO_2-Ta_2O_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 ($IrO_2 \cdot 2H_2O$) or iridium(III)-acetylacetonate ($Ir(acac)_3$).

The formation of IrO_2 and Ir by thermal decomposition of $IrO_2 \cdot 2H_2O$ 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, $IrO_2 \cdot 2H_2O$ was amorphous, as found by XRD [1]. SAED pattern of that sample furthermore evidenced the presence of amorphous material (Fig. 1). Raman spectrum of $IrO_2 \cdot 2H_2O$ 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 $IrO_2 \cdot 2H_2O$ 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 grouth 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 $IrO_2 \cdot 2H_2O$ and $Ir(acac)_3$ in air.

[1] S. Musić, S. Popović, M. Maljković, Ž. Skoko, K. Furić, A. Gajović, "Some factors influencing thermochemical formation of IrO_2 and Ir", Materials Letters 57 (2003) 4509– 4514.

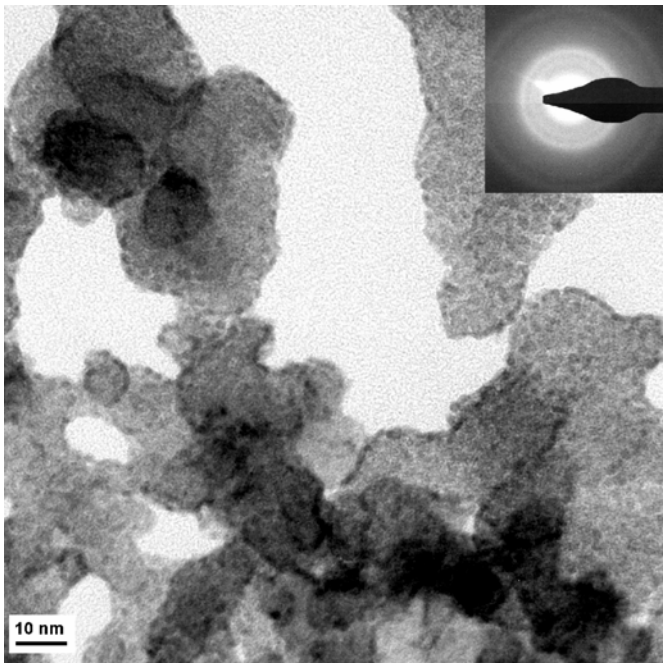

Figure 1: TEM and SAED pattern of amorphous $IrO_2 \cdot 2H_2O$ particles.

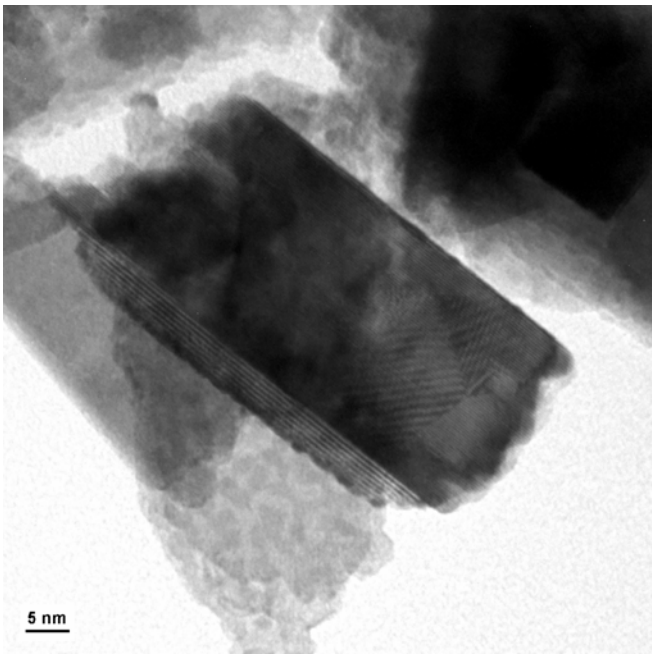

Figure 2: Nanosize IrO_2 particle obtained by heating $IrO_2 \cdot 2H_2O$ at 600 °C.

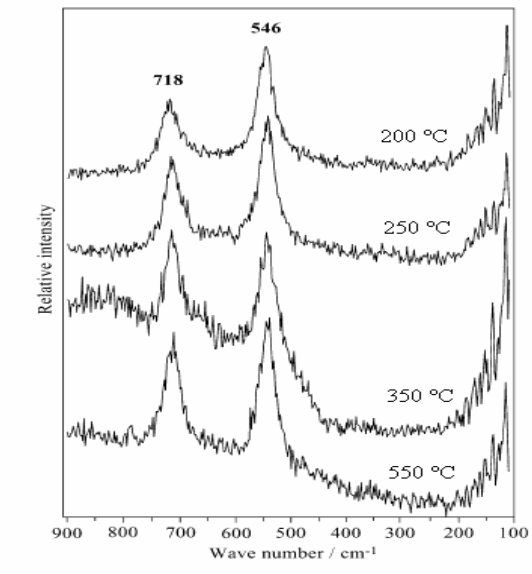

Figure 3: Room temperature Raman spectra of IrO_2, prepared by heating $Ir(acac)_3$. Temperature of IrO_2 preparation are denoted above spectra.