Synthesis of Irregular Tantalum Pentoxide (Ta$_2$O$_5$) Microparticles by Direct Thermal Oxidation of Ta Foils in Atmospheric Oxygen

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Abstract. In this work, Tantalum pentoxide (Ta$_2$O$_5$) microparticles were achieved by one-step thermal oxidation of Tantalum (Ta) foils under 600 °C for 6 h. The effect of time and temperature was explored in the process (50 to 600 °C, 1 to 6 h). Thus, Ta foil was chemically cleaned with nitric and hydrochloric acid and then was immersed in water; finally it was dried with Nitrogen flux. The foils were isothermally oxidized in a horizontal furnace with 21 wt. % Oxygen atmosphere in a constant flux of 20 L/min. The x-ray diffraction, scanning electron microscopy, Raman and energy dispersive x-ray spectroscopy led to the conclusion that formation mechanism of microparticles is mainly constituted by lattice parameters mismatching between Ta and Ta$_2$O$_5$ and crystallite size difference. Along the oxidation process at 600 °C, the phase transformation across time carries defect concentrations on entire material experimentally demonstrated by Ta$_2$O$_5$ Raman shift and then the sample is broken in irregular shape. As oxidation time reaches 6 h value, phase transformation in Ta foil causes mismatching that firstly diminishes crystallite size, then evolves to cracks and finish by the formation of the particles in the micrometer order size.

Keywords: phase transformation, Ta$_2$O$_5$ Raman shift, formation mechanism, lattice mismatching

1. Introduction
Tantalum pentoxide (Ta$_2$O$_5$) is a biocompatible and semiconductor material. It has been proved to have many promising applications such as corrosion resistance covering material for biomedical applications [1] and dielectric applications by a thin film on semiconductors [2]. Among different morphologies, Tantalum oxide particles have potentials applications for angiography as well as RES-targeted imaging to improve the detection of metastases in the liver and lymph nodes [3]. It is possible to make compounds with Ta$_2$O$_5$ to improve the surface bio-performances of polyimide (PI), the surface roughness, hydrophilicity, surface energy and protein adsorption as well as apatite mineralization of STPC in simulated body fluid were significantly enhanced [4]. Gram-scale synthesis of uniform-sized TaOx particles was achieved using a simple microemulsion method in the work of Myoung Hwan et al [4]. As it was reported by Krishnaprasanth and Seetha Ta$_2$O$_5$ particles can be prepared by thermal decomposition method without using any solvents [5]. Ta$_2$O$_5$ nanoparticles with the size in the range of 20-50 nm were obtained via a chemical route described in the work of Huang and Hsieh [6]. Among methodology to synthesized metal-base micro-structured materials, heterogeneous nucleation...
promoted by thermal oxidation has been proven to be an accessible method to produce uniform oxides-phase from highly pure metal foils in an extensive area. [7]

This research contributes to the exploration of accessible methodologies for obtaining highly pure microparticles with a single orthorhombic tantalum pentoxide phase. In this work, a Tantalum (Ta) foil was chemically cleaned with hydrochloric and nitric acid solutions, then Ta foil was rinsed in water and dried with Nitrogen flux. Afterword, the plate was thermally oxidized in a 21 wt. % Oxygen atmosphere for 1 to 6 h at 50 °C to 600 °C range. Ta2O5, microparticles obtained at 600 °C were structural and morphologically characterized. The formation mechanism of Ta2O5 microparticles is discussed based on results.

2. Materials and methods

2.1 Chemicals
The Tantalum (Ta, 99.99 %), nitric acid (HNO3, 70 %), hydrochloric acid (HCl, 70 %), deionized water (H2O, 18 MΩ) and methanol were commercially acquired from Sigma Aldrich and used without further purification.

2.2 Microparticles synthesis
To obtain Tantalum oxide, the Ta foil was cut small sheets (0.5 x 0.5 cm). Afterward, the Ta sheets were chemically cleaned with HCl 0.1 M solution for 1 min to remove organic impurities and then with HNO3 0.1 M solution for 1 min to remove metallic oxide impurities, finally deionized water was employed to remove residues of acid solution and then dried with Nitrogen flux to avoid further oxidation. Once Ta foils were cleaned, they were oxidized in a horizontal furnace in a 21 wt. % Oxygen atmosphere at constant rate of 20 L/min. In order to study the effect of heat in phase structure, a range of temperature from 50 to 600 °C was employed in the synthesis with 50 °C as increasing step. The effect of time in morphological properties was studied from 1 h to 6 h with a 30 min as increasing time. To study the reproducibility, each condition of synthesis was performed by triplicate in separate experiments.

2.3 Characterization
The phase in samples was characterized by x-ray diffraction (XRD) using a x’pert Panalytical diffractometer (Cu kα = 1.5418 Å), while morphological properties of the samples were obtained by electron microscopy (SEM) using a JSM-7800F field emission scanning electron microscope (FE-SEM). To determine the pollutants present in micro-particles, an energy dispersive x-ray spectroscopy (EDS) was performed by an Eurotherm coupled system in the FE-SEM. The defects present in the condition of synthesis were analysed in the corresponding vibrational modes in Raman spectroscopy recorded by INTEGRA Spectra equipment with wavelength excitation of 532 nm.

3. Results
The structural features of samples after thermal oxidation on Ta foils were analysed by XRD pattern (Figure 1). Based on temperature exploration, it was observed that cubic Ta phase remains present till 300 °C is reached. The pattern obtained for samples processed between 50 °C and 300 °C is shown in Figure 1a. For this pattern, cubic Ta phase was identified by matching the picks at 38.47, 55.55 and 69.60 degrees with (011), (002) and (112) planes, respectively (Reference code: 98-007-6014). Single orthorhombic Ta2O5 phase was achieved when samples were processed at 600 °C. It was confirmed by matching pick position at 22.84, 28.29, 36.66, 46.66, 49.78, 50.68, 55.74, 58.52, 63.65 and 71.34 degrees with (100), (011), (111), (200), (020), (013), (202), (022), (122) and (213) planes for the corresponding phase in the pattern shown in Figure 1b, respectively (Reference code: 98-004-3498). The lattice parameters were computed by Rietveld approaching in High Score Plus software, obtaining as results for the Ta phase a set of values of a = b = c = 3.30 Å and for the Ta2O5 phase a collection of values of a = 3.89 Å, b= 3.66 Å and c= 6.20 Å. Based on these results, lattice for each face was simulated (inserts in Figure 1). As it can be seen, the full width at the half maximum (FWHM) in the
Ta₂O₅ phase is bigger than that from the Ta phase, thus not just the lattice parameters have great difference but crystallite size is smaller in Ta₂O₅ phase.

Figure 1. The normalized XRD pattern of samples thermally oxidized from (a) 50 to 300°C and (b) at 600 °C. Inserts show the simulated unit cell for (a) Tantalum and (b) orthorhombic tantalum pentoxide, respectively.

Samples with single Ta₂O₅ phase (obtained at 600 °C) were chosen to be characterized by FE-SEM (Figure 2). The morphological properties obtained after 1 h of temperature exposition, results in nanopattern on surface with high crystallinity (Figure 2a and 2d), these is in good agreement with the reports [2]. Then, after 3 h of oxidation process, it can be seen microstructure changes on surface, crack appearance (pointed by blue arrow in Figure 2b) and pore generation (pointed yellow circles in Figure 2e). After 6 h of treatment the foil has completely cracked, allowing the formation of microparticles (Figure 2c). By analyzing the surface of one Ta₂O₅ microparticle, boundaries have a regular morphology (pointed by blue arrow in Figure 2f). This suggests that material cracking to drive particles formation is due to these particular sites, thus they play an important role in process.

Figure 2. Ta foil imaged by FE-SEM after oxidation at 600 °C for (a) 1 h, (b) 3 h and (c) 6 h. The (d), (e) and (f) show close view of (a), (b) and (c) images, respectively. Insert in (f) is an amplified section.

EDS was performed on an extensive area of samples. As it can be seen in Figure 3a the energy values for Ta and O are the unique elements present in the samples (besides that from Carbon due to tape to
hold the sample in FE-SEM). Raman spectroscopy is shown in Figure 3b, where the Raman shift are in good agreement with those reported for Ta$_2$O$_5$ in literature (see Table 1) [8]. The modes associated with the O – Ta – O and O – 3Ta binding are located at range from 150 to 400 cm$^{-1}$ (i and ii), to O – 3Ta stretching modes are located between 450 and 800 cm$^{-1}$ (iii, iv and v) and those associated to O – 2Ta stretching appear from 800 to 1000 cm$^{-1}$ (vi and vii). Vibrational modes shifting between samples in synthesized at different times, shows diverse defect amount in similar way it has been prove [9].

![Figure 3](image3.png)

**Figure 3.** The (a) EDS spectra and (b) Raman shift of samples synthetized at 600 °C for 1 (red), 3 (blue) and 6 h (black).

**Table 1.** The Raman shift of Ta2O4 samples synthetized at 1, 3 and 6 h.

| Vibrational mode | 1 h (cm$^{-1}$) | 3 h (cm$^{-1}$) | 6 h (cm$^{-1}$) |
|------------------|----------------|----------------|----------------|
| i                | 198.17         | 196.51         | 199.84         |
| ii               | 251.42         | 246.43         | 248.76         |
| iii              | 487.72         | 496.04         | 491.05         |
| iv               | 612.52         | 619.18         | 620.84         |
| v                | 707.38         | 702.38         | 712.37         |
| vi               | 843.83         | 845.49         | 850.48         |
| vii              | 950.33         | 958.65         | 973.62         |

The formation mechanism of micro-particles can be explained based on results. First, when Ta$_2$O$_5$ nucleus are formed, defect induction and inner stress start in Ta crystal (Figure 4a), then Ta$_2$O$_5$ phase grows and drives defect concentration (Figure 4b), once phase transformation has finished polycrystalline Ta$_2$O$_4$ is resulting with inner stress due to defect concentration generated previously, thus material cracks and leave the formation of micro-particles.

![Figure 4](image4.png)

**Figure 4.** Scheme of the formation mechanism stages of Ta$_2$O$_5$ microparticles synthesized at 600 °C across time (a) initial, (b) middle and (c) final stage.
4. Conclusion
In summary, Ta$_2$O$_5$ microparticles were synthesized successfully by simply thermal oxidation on Ta foil. The Ta$_2$O$_5$ microparticles with a homogeneous orthorhombic phase were achieved at 600 ºC and 6 h. According to vibrational spectroscopy results, the Ta$_2$O$_5$ formation mechanism is strictly related to defect concentration due to lattice mismatching between Ta and Ta$_2$O$_5$ in the oxidation process. This work gives a proposal for accessible methodology for obtaining Ta$_2$O$_5$ microparticles. It is recommended that future work stay focused on introduce an extra parameter to take control of size and shape.

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