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SYNTHESIS AND CHARACTERIZATION OF Ta_2O_5 NANOPARTICLES BY SOL-GEL TECHNIQUE IN A POLYSACCHARIDE MATRIX

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Metal oxide fine particles are widely used in industrial applications such as catalysts, pigments, etc. In this work, Ta_2O_5 nanoparticles were synthesized by controlled hydrolysis of tantalum oxide in presence of a polysaccharide network (1-3 linked β-D galactapyranose and 1,4 linked 3,6 anyhdro-α-L-galactopyranose). Spherical crystalline nanoparticles in the range of about 1-8 nm were obtained when the polysaccharide was used. The obtained nanoparticles were characterized by atomic force microscopy (AFM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and particle size and distribution analysis.

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1. Introduction

Tantalum oxide is of great importance in materials science and nanotechnology because of their characteristics and properties . Recent progress in the synthesis and characterization of nanowires, nanoparticles and nanorods has been driven by the need to understand the novel physical properties of one-dimensional (1-D) nanomaterials, and their potential applications in constructing nanoscale electronic and optoelectronic devices [1]. Nanostructured materials of transition-metal oxides such as tantalum, titanium, and vanadium oxides are generally accepted as the next generation materials in electronics [2-5] and advanced catalysts[6-7]. Tantalum (V) oxide has attracted considerable attention for its application in microelectronics, for example, in integrated capacitors, due to its dielectric constant [8], in advanced catalysts [9], storage energy[10]. Nanoparticles of Ta_2O_5 has also been used as biomaterials in filled resins because of its low toxicity resulting from its high oxidation state, chemical inertness and biocompatibility [11-12]. Despite such potential applications, there are only a few reports on the preparation of Ta_2O_5 at nanometer scale. These reports include the use of organogelators as a structure directing agent for nanotubes preparation. Chan et al.[13] prepared Ta_2O_5 nanoparticles by non aqueous condensation of tantalum ethoxide. Akihito et al. [14] reported the use of vapor-solid reaction methods for the synthesis of Ta_2O_5 nanoparticles. The sol-gel and spin coating methods have also been used for the production of Ta_2O_5 thin films [15]. This method is promising for new materials at the nanometer scale [16]. An advantage of the sol-gel method over other methods such as hydrothermal synthesis, chemical vapor deposition etc., is that it produces materials with high surface area [17]. The main goal of this work is to present an easy route for the synthesis of spherical Ta_2O_5 nanoparticles by

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sol-gel synthesis, facilitated by a linear polysaccharide such as β-D galactapyranose and 1,4 linked 3,6 anyhdro-α- L- galactopyranose in order to promote a controlled growth of spherical nanoparticles.

2. Experimental Section

The precursor material tantalum (V) ethoxide $(CH_3CH_2O)_5$ Ta (1M, in ethanol, pH = 7.0) was solution coated into a Ta_2O_5 metallic solution followed by drying and calcination process. For gel formation, a solution of 99% chemically pure grade polysaccharide (1-3 linked β-D galactapyranose and 1,4 linked 3,6 anyhdro-α-L-galactopyranose) was used. Approximately 200 µl of the solution of polysaccharide was warmed up to 40 ºC for about 30 minutes. Then 200 µl of tantalum ethoxide was added to it dropwise. In this way, the growth of metallic precursor was controlled by the polysaccharide network. The gel was then placed in 1 ml tube and centrifuged at 12,000 rpm for 10 minutes at 28 ºC. The concentrated gel was poured off and the precipitate washed several times with deionized water to ensure complete elimination of the gel. It was further centrifuged at 12,000 rpm for 10 minutes to recover the powder precipitate. This was followed by a 48 hours incubation at 28 ºC to evaporate any residual water. The powders were then calcined in a laboratory muffle furnace at 800 ºC for 2 hours. Morphology observation and elemental EDS analysis of the obtained particles were made by AFM Nanosurf and energy dispersive spectroscopy model JEOL JSM-5800 LV/EDS respectively. TEM images were obtained in a Phillips CM-200 transmission electron microscope at an accelerating voltage of 200 kV. The crystallinity of calcined powders were analyzed by XRD using a CuK(α) source at 0.1542 nm using a Phillips X'PERT X-Ray difractometer.

3. Results and discussion

The polymer gel was prepared using a method similar to that described by Sugimoto et al. [18]. Fig. 1, shows the AFM micrograph of the prepared tantalum oxide nanoparticles. Most of the particles were agglomerated to a spherical shape, possibly due to the network structure of the polysaccharide.

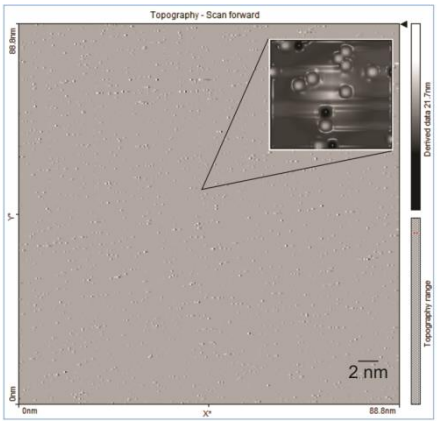

Fig.1. AFM micrographs showing the shape of the Ta_2O_5 nanoparticles formed in presence of polysaccharide compound.

3.1 Particle size distribution

Fig. 2, shows the particle size distribution, derived from AFM observation. It shows that most of the nanoparticles are in the range of about 1 to 8 nm approximately. Our results are

comparable to particle sizes of less than 10 nm reported using methods such as hydrogen arc plasma [19].

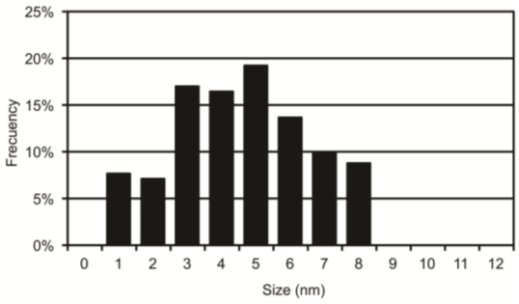

Fig. 2. Particle size distribution of Ta_2O_5 nanoparticles.

The shape and size of the nanoparticles could be induced and controlled by the polymeric network of gel in liquid phase. When the tantalum precursor is added, the particles grew in a disordered way. In order to ascertain if the polysaccharide solution controls the morphology of the nanoparticles, a control experiment was carried out in absence of polysaccharide.

3.2 Characterization of Ta_2O_5 nanoparticles by Atomic Force Microscopy.

The result presented in Fig. 3 confirmed that the obtained particles were large (up to about 60 nm) with irregular shape and disordered. Thus, in the absence of the gel polymeric network, the metallic precursor tends to homogenize itself and condense irregularly. Therefore, the polysaccharide network is useful for the growth, control and formation of spherical nanoparticles.

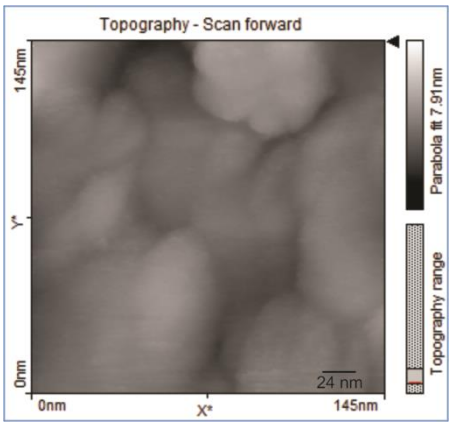

Fig. 3. AFM micrographs showing large Ta_2O_5 particles of irregular shape formed in absence of polysaccharide compound.

The sol-gel process offers the advantage to use metallic alkoxides and control the reaction rates by controlling the hydrolysis and condensation by chemical means and not by colloidal chemistry since the alcoxy group OR (R = organic group saturated or unsatured) is a strong π bond donor and stabilize the highest oxidation state of the metal. As particles grow and move against each other, condensation occurs, forming macroparticles. Upon addition of the polysaccharide and mixing the solution results in beginning of the gelation process (this is the so called gelation point). From this point, the conversion sol-gel is gradual and more and more particles become interconnected in the polysaccharide network. In the present case, the use of polysaccharide (at a given concentration) helps in controlling the particle size. This could be due to the fact that the particles could pass through the OR alcoxy groups and the anionic groups of the polysaccharide before the gel gets polymerized [20].

3.3 Characterization of Ta_2O_5 nanoparticles in Transmission electron microscope.

Fig. 4 shows a TEM image of particles, where the chemical composition of one nanoparticle was analyzed by EDS point analysis.

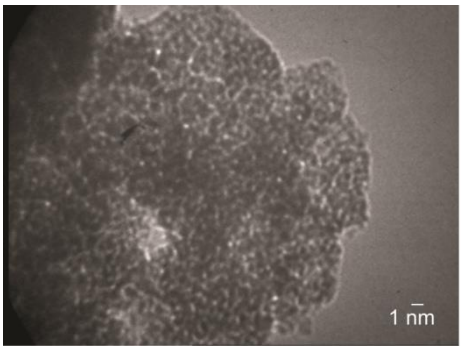

Fig. 4. TEM image of spherical Ta_2O_5 nanoparticles.

3.4 Characterization by EDS

The EDS spectrum (Fig. 5) indicates the presence of Ta and O as the main elements, with no indication of any contamination.

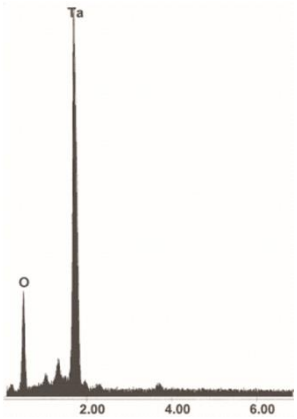

Fig. 5. Typical EDS spectrum of the Ta_2O_5 nanoparticles obtained.

3.5 X-Ray Diffraction pattern.

Fig. 6 shows the XRD diffraction pattern of Ta_2O nanoparticles formed in presence of polysaccharide compound. It clearly shows peaks of (001), (100), (101), (002), (110), (102), (200), (201) planes. The crystallite size was measured using a new graphical method (X' Pert Data Viewer in a Diffractometer X' Pert) at 40 kV and 30 mA. The crystalline structure of Ta_2O_5 phase was identified as orthorhombic structure.

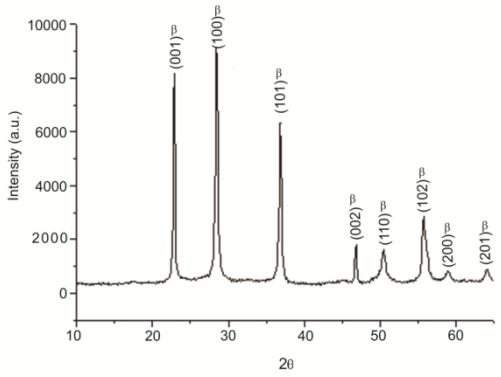

Fig. 6.- X-ray diffraction pattern of sol-gel prepared nanoparticles of Ta_2O_5 calcined at 800 °C for 2 h obtained, using a CuK(α) source at 0.1542 nm.

4. Conclusions

Tantalum oxide nanoparticles of spherical shape in the range from 1-8 nm were obtained by a sol-gel process facilitated by the presence of a linear polysaccharide. EDS analysis on the nanoparticles indicated mainly the presence of Ta and O. The method used involved several steps: 1) separation of the lineal chains of polymer by hydrolysis, 2) formation of a polymeric porous network, 3) addition of the metallic precursor to the polymeric network, 4) formation of nanoparticles, 5) recovery of nanoparticles by centrifugation, and 6) precipitate calcination. This method offers an easy route to obtain spherical Ta_2O_5 nanoparticles and could be extended toward the synthesis of other transition oxides. The crystallinity and particle size distribution of the Ta_2O_5 spherical nanoparticles are promising for application in fine biocatalytic systems, materials science, for inhibition or acceleration of chemical reactions at molecular level, where the shape and crystallinity plays a role in the binding of the inorganic molecules.

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