



## Review

## Nanosized tantalum based materials – synthesis and applications

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## ABSTRACT

The excellent properties and enormous applications of tantalum have attracted much interest in understanding their miniature, such as nanosized tantalum materials, because the nanoscale alters their properties significantly. This review aims to provide a comprehensive summary of the up-to-date research results on the various synthetic procedures of nanosized tantalum materials, including naked tantalum nanoparticles, nanocomposites, and core/shell nanoparticles. In addition to their synthetic procedures, their utilization towards a variety of applications, such as photocatalytic hydrogen evolution, photocatalytic degradation of organic pollutants, osteological applications, and fabrication of solar cells, were also discussed in this article. The variation in the reaction conditions, such as concentration, reaction temperature, and reaction time, etc., can substantially affect the morphology, particle size, size distribution, and crystallinity. Although this review confines to the materials containing nanosized tantalum particles, the information provided will be of great help in various disciplines.

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## 1. Introduction

Owing to the unique physical properties as well as the significant role in a variety of potential applications, tremendous attention towards the research on oxide semiconductors from the scientific community is being devoted for the past several decades [1,2]. Among various transition metal oxide semiconductors, tantalum ( $\text{Ta}_2\text{O}_5$ ) is a more promising functional semiconductor which possesses peculiar properties, such as wide band gap  $E_g$  of 4.0 eV, high dielectric constant of  $\sim 50$ – $70$ , high refractive index of  $\sim 2.125$ , high resistivity, good breakdown field strength, high ionic conductivity of  $\sim 10^{-5}$ – $10^{-9}$  S/cm, good thermochromism as well as electrochromism, high temperature piezoelectric properties, high-coloration-efficiency, high biocompatibility, low leakage current of  $\sim 2 \times 10^{-8}$  A/cm<sup>2</sup> at 1 MV/cm, low internal stress, low light absorption coefficient, and good thermal, mechanical, and chemical stability [3–11]. Due to these attractive properties, tantalum was found with various applications in high-density dynamic random-access memory (DRAM) devices as storage capacitors, surface acoustic wave devices such as band-pass filters, microelectronics devices as high-k gate insulator, electroluminescent display devices as insulator, various types of mechanical sensors, humidity sensors, solid-state ion sensors, gas sensors, complementary metal-oxide-semiconductor (CMOS) field-effect transistors, corrosion protection coatings for biomedical implants, surgical instruments and evanescent optical sensors with high surface sensitivity, anti-reflection coatings for lenses and solar panels, photocatalysis, thermochromic 'smart windows', multilayer interference filters, and piezoelectric sensors [8–15].

Since the bulk tantalum particles own excellent peculiar properties as well as immense applications, a fascination towards understanding those particles in the nanorange arises in the recent years. In general, the physicochemical and optoelectronic properties get modified while reducing the particle sizes into nanoscale especially due to their increase in surface area. Those unique properties of nanoparticles have led to enhanced applications compared to bulk tantalum [16,17]. Therefore, nanosized  $\text{Ta}_2\text{O}_5$  materials with various morphologies are receiving a significant consideration from both fundamental research and practical applications [5,18].

In this review, the syntheses of nanosized tantalum materials, including (i) naked tantalum nanoparticles with different morphologies such as nanospheres, nanorods, nanotubes, nanofibers, nanowires, nanoneedles, round shaped particles, nanoblocks, etc., (ii) nanocomposites containing tantalum nanoparticles with non-metal, metal, semiconductor, organic heteropoly acids, and (iii) core/shell nanoparticles, were discussed using the different synthetic methods available in the literatures. Furthermore, this review discusses the utilization of these nanosized tantalum materials in the field of photocatalytic hydrogen evolution, photocatalytic degradation of organic pollutants, osteology, and its use for dye sensitized solar cells.

## 2. Synthesis of nanosized tantalum materials

The growth of novel nanoscale materials not only depends on their applications, but also on the better understanding of the

synthetic methods which modulate the structural morphology, particle size distributions, and composition. This section reviews the several synthetic methods recently developed to synthesize various tantalum nanomaterials for tuning the morphology, size, and crystallinity.

### 2.1. Naked tantalum nanoparticles

This section discusses the synthesis of different morphological naked tantalum nanoparticles by various synthetic methods, such as sol-gel process, solvothermal, template, chemical route, chemical vapor deposition, and anodization along with the variation in their size, shape and as well as crystallinity with different calcination temperature and time (Table 1).

#### 2.1.1. Sol-gel process

Among the various synthetic techniques for preparing nanoscale oxides, the most widely used "bottom up" wet chemical method is the sol-gel process since it results in the formation of uniform ultra-fine porous powder with ultra-high purity and can be scaled up to accommodate industrial-scale production at a low cost. Typical sol-gel synthesis is a combination of several chemical reactions involving the hydrolysis of the precursors usually alkoxides followed by inorganic polymerization to form liquid "sol", solidification of the formed sol into the gel followed by syneresis and Ostwald aging [16,19–26]. This simple sol-gel method was employed to synthesize tantalum nanoparticles by various research groups [16,20,27–35].

Using sol-gel method, Romero et al. [27] synthesized  $\text{Ta}_2\text{O}_5$  nanorods by incubating the gel formed from the mixture of  $\text{Ta}(\text{OC}_2\text{H}_5)_5$  in ethanol and poly L-lysine in water at 4 °C in ice for 10 days and then followed by calcination at 700 °C for three hours. Here poly L-lysine, natural homopolymer of the amino acid L-lysine, acted as a structure directing agent to form orthorhombic  $\beta$ -phase  $\text{Ta}_2\text{O}_5$  nanorods with diameter of 20 nm. Zhu et al. [28] successfully synthesized  $\text{Ta}_2\text{O}_5$  nanoparticles using sol-gel method by drying the 24 h gelatinized mixture of  $\text{TaCl}_5$ -butanol solution, diethanolamine as stabilizer and water as a hydrolyzing agent. The as-synthesized nanoparticles were further calcined at different temperatures from 400 °C to 800 °C as well as for different calcination times from 2 h to 24 h. The  $\text{Ta}_2\text{O}_5$  nanoparticles calcined at 400 °C as well as less calcination time (2 h) were amorphous in nature whereas prolonging the calcination period for 24 h or increasing the temperature to 800 °C not only increases the perfectness in the crystalline phase of  $\text{Ta}_2\text{O}_5$ , but also increases the size (Table 1, 2). In particular, the crystallinity has arisen on the particles calcined above 650 °C after 4 h.

Extending the synthesis procedure towards surfactant-assisted sol-gel process shows several advantages, such as excellent control over crystal size as well as crystal shape, narrow size distribution, low agglomeration tendency, and good redispersibility [20]. Using surfactant-assisted sol-gel process, Sreethawong et al. [29,30] synthesized mesoporous  $\text{Ta}_2\text{O}_5$  nanoparticles by gelling the sol synthesized by stirring  $\text{Ta}(\text{OC}_2\text{H}_5)_5$ /acetylacetone (ACA) mixture at a ratio of 4:1 with aqueous laurylamine hydrochloride (LAHC) solution (pH 4.2) at 80 °C for one week and thus formed zero gel was calcined at different temperatures in the range of 500–800 °C

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