Chemical Engineering Journal 321 (2017) 447–457

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

An atmospheric pressure microplasma process for continuous synthesis of titanium nitride nanoparticles

Liangliang Lin [a], Sergey A. Starostin [b], Qi Wang [a,*], Volker Hessel [a,*]

[a] Micro Flow Chemistry and Process Technology, Chemical Engineering and Chemistry Department, Eindhoven University of Technology, The Netherlands
[b] FUJIFILM Manufacturing Europe B.V, Tilburg Research Labs, P.O. Box 90156, Tilburg, The Netherlands

HIGHLIGHTS

- Microplasma process is developed for continuous, one pot synthesis of TiN NPs.
- The obtained NPs are extremely small, uniform and have polycrystalline nature.
- The admixture of H_2 during synthesis process can reduce the oxidation of TiN NPs.
- Comparative analysis of key parameters among competing technologies is carried out.
- Microplasma array design is shown as a promising way to scale up the throughput.

ARTICLE INFO

Article history:
Received 18 January 2017
Received in revised form 25 March 2017
Accepted 27 March 2017
Available online 28 March 2017

Keywords:
Microplasma
Atmospheric pressure plasma
Nanomaterial synthesis
Titanium nitride

ABSTRACT

This research studies a continuous process for the direct synthesis of titanium nitride nanoparticles assisted by an atmospheric pressure microplasma. Titanium tetrachloride ($TiCl_4$) is used as precursor and nitrogen is used as reacting gas. Composition and microstructure analysis (SEM, EDX, TEM, HRTEM, XRD and XPS) of the synthesized nanoparticles reveals that nanometer-sized titanium nitride (TiN) with polycrystalline nature can be directly prepared by the studied process, and the admixture of H_2 gas in plasma during synthesis process can be an effective way to reduce the oxidation of TiN nanoparticles. The influence of the dissipated power and H_2 concentration on the optical emission spectra of the microplasma in the operating reactor is investigated. The characteristics gas temperature of the plasma filament is estimated from the emission averaged spectra. A hypothesized mechanism of TiN synthesis in microplasma is illustrated, and comparisons with preceding researches are carried out. Based on process analysis and experimental results, the feasibility of the upscale towards industrial level production is discussed.

1. Introduction

Due to the superior thermal stability, high wear resistance associated with extreme hardness and good corrosion resistance, TiN nanostructures are widely used as coating material [1,2], cermet [3], cutting tools [4], refractory material [5] and electrodes of electrochemical capacitors [6,7]. In recent years TiN nanoparticles were also found to be a promising catalyst support in battery application for their excellent conductivity [8]. Moreover, an emerging application of nanostructured TiN lies in the field of plasmonics, where transition metal nitrides are expected to bring technological breakthrough [9]. Traditionally gold and silver nanoparticles are selected as plasmonic materials due to their strong plasmonic response in the near IR and visible region in conjunction to extensively-studied and well-developed colloidal assembly methods. However, disadvantages of noble metals are in high costs, relatively low melting point and conduction electron mobility, rendering them unstable for high temperature electronic and photothermal devices [10]. Being similar in optical properties to gold nanoparticles, nanostructured TiN as an alternative plasmonic material can eventually replace and outperform gold due to its low cost accompanied by durability and chemical stability at high temperatures [11].

Currently, TiN nanoparticles are produced either by plasma assisted methods, such as thermal plasma approach [12–15], plasma spray [16], RF plasma [17,18] and microwave plasma [19]; or by non-plasma methods, such as direct nitridation of TiO_2 [20], chemical vapor deposition [21], benzene-thermal route

* Corresponding authors.
E-mail addresses: q.wang0207@gmail.com (Q. Wang), v.hessel@tue.nl (V. Hessel).

http://dx.doi.org/10.1016/j.cej.2017.03.128
1385-8947/

[22], hydrazide sol-gel process [23], carbon thermal reduction [24] etc. Although significant progress has been achieved in TiN nanostructure synthesis and its application, some issues still remain to be addressed.

For technologies without plasma employment, fine quality TiN nanomaterial can be prepared when the starting materials were properly chosen, with processes being well controlled [22–24]. However, these are generally multi-steps methods and need complex manipulation, involving catalysts, toxic stabilizers, surfactants or reducing agents in most cases. Moreover, post treatments such as separation, washing, heating or annealing to improve particle purity and crystallinity are always required, being time and energy consuming. As to the plasma assisted process in nanomaterial synthesis, its remarkable benefits are in being simple, continuous, clean and highly efficient. Due to the presence of high density reactive species, plasma can significantly accelerate reactions rates and even stimulate the chemistries that are hardly realized by non-plasma methods [25–27]. Once precursors are introduced into the plasma, they will be dissociated rapidly and generate nanoparticles in a one pot synthesis way. The plasma-assisted process also does not involve extra chemicals or catalysts as most wet chemistry methods do, and post treatments are not necessary, ensuring a clean and efficient synthesis. However, the merits of conventional plasma processes are often offset by low pressure operation and high power consumption, which limit their industrial application. The produced nanoparticles are usually relatively large in average and characterized by the broad size distribution, for it is difficult to sustain a uniform temperature and to avoid coagulation in bulk plasma process. Fortunately, those problems could be addressed by microplasma, which is a new generation technology for nanomaterial synthesis [28–31]. As compared to bulk plasma methods, one notable advantage of microplasma is that discharges can be generated and maintained stably at atmospheric pressure, thus reducing the costs by omitting need for expensive vacuum equipment [32]. On the other hand, high pressure operation also contributes to increase in radical densities and non-equilibrium chemistry enhancement, allowing for efficient, non-thermal dissociation of molecular gases or precursor vapors at higher reaction rates [33,34]. Another advantage of microplasmas is that due to their microscale geometry, high surface-to-volume ratio can be obtained.

For such geometries the Joule heating in plasma is balanced by the efficient thermal conductivity and does not lead to the excessive temperature rise, making it attractive for the synthesis of temperature sensitive materials especially bio-materials. The confined spatial scale also ensures short residence time and a narrow residence time distribution (RTD), which helps to control particle nucleation and growth. Meanwhile, it also leads to high energy density, making it possible to initiate reactions even at very low power.

With the motivation to design a continuous and low-cost process to prepare high quality TiN nanoparticles, the main focus of the present work is to show that titanium nitride nanoparticles can be successfully synthesized by a home built atmospheric pressure microplasma setup, at extremely low plasma power consumption. The microplasma was characterized by optical emission spectroscopy and electrical measurements. A detailed study on chemical composition, microstructure and morphology of the synthesized products is carried out employing various analytical methods. Besides, by comparing and analyzing the advantages and disadvantages of the microplasma process with other methods for TiN nanoparticles synthesis, this study also demonstrates the feasibility of scaling up this process to industrial level production, using a microplasma array reactor. To the best of our knowledge, it is the first report on producing TiN nanoparticles by a microplasma process.

2. Experimental

2.1. Experiment setup

In this research a home-built atmospheric pressure reactor was used for the synthesis of TiN nanoparticles, as illustrated in Fig. 1. $TiCl_4$ (≥99.0%, Sigma-Aldrich) was employed as the precursor being injected into the plasma with continuous argon flow through the line 1. The bubbler vessel containing liquid precursors was installed on the top of an electronic scale (Sartorius, type R 300 S) to quantify the $TiCl_4$ mass flow rate. A separate argon flow was used as a dilution gas to control the precursor concentration and maintain a constant total gas flow rate (line 2). To study the influence of H_2 on precursor dissociation process and the synthesized products, another pipeline was also constructed (line 3). Besides, a continuous N_2 flow was supplied as the reacting gas (line 4). All gas flows were individually controlled by mass flow controllers (MFCs) and mixed before being injected into the reactor. Plasma was formed between a stainless steel (SS) capillary tube (Sigma-Aldrich, O.D. = 1.6 mm, I.D. = 500 μm) and a SS mesh (Wire Weaving Co. Dinxperlo, Warp & Weft opening: 500 × 500 μm), with a gaseous gap of 2 mm, sustained by a commercial DC power supply (Matsusada Precision, Model AU-10R30). The experimental values of microdischarge power, current and voltage were automatically logged using a LabVIEW based program. A very fine SS mesh (Wire Weaving Co. Dinxperlo, Warp & Weft opening: 77 × 77 μm) was placed downstream the aerosol, on a small homemade SS table, to collect products. The electrodes and substrate were encapsulated within a quartz reactor to form a "closed" type system, being isolated from environment. In order to prevent condensation of the precursor vapor the reactor was placed inside an oven to sustain uniform temperature. Meanwhile, the oven enclosure also served as an additional protection from the risks of direct contact with the reactor and exposure to high voltage circuitry. Gas sensors coupled with a control system were designed as a safety measure to detect gas leakage. Due to the high degree of constructive and operational flexibility, the setup can be viewed as a reliable multi-functional system for nanomaterial synthesis.

2.2. Synthesis of titanium nitride nanoparticles

As reported in preceding researches, higher plasma power contributed to precursor dissociation rate enhancement, while also resulted in larger-sized particles [35,36]. Therefore the plasma power control allows for tunable precursor dissociation rate as well as particle size tailoring during synthesis process. In the described setup variation of the generator output voltage is the most convenient way to control the plasma power. For the majority of reported experiments the output voltage was fixed at 4500 V to provide a moderate dissociation rate as well as fine nanoparticles. In order to prevent precursor condensation in the pipelines, the oven temperature was set at 353.15 K during the experiments. The reactor was flushed with Ar before operation to remove oxygen impurities. The total gas flow rate was fixed at 110 ml/min, enabling us to maintain a constant residence time. In every experiment the plasma was switched on for a certain time (20 min) to ensure stable conditions before adding the precursor. After a desired process time (40 min), the plasma was switched off and the SS mesh was carefully taken out by a tweezers, with obtained products collected into a small bottle by carefully knocking the mesh. The feeding rate of the precursor was quantified by measuring the precursor holder weight before and after experiment. Table 1 lists the processing parameters for the synthesis of TiN nanoparticles. In most cases, experiments were carried out at the condition 1 to produce TiN nanoparticles with N_2 and $TiCl_4$. Fur-