



# Preparation of new titanium nitride-carbon nanocomposites in supercritical benzene and their oxygen reduction activity in alkaline medium



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## ARTICLE INFO

### Article history:

Received 3 December 2014

Received in revised form 17 February 2015

Accepted 24 February 2015

Available online 25 February 2015

### Keywords:

Titanium nitride-carbon nanocomposite

Supercritical benzene

Oxygen reduction reaction

## ABSTRACT

Titanium nitride-carbon nanocomposites are synthesized by the reaction of  $\text{TiCl}_4$  and  $\text{NaN}_3$  in supercritical benzene medium that also serves as a carbon source. The as-prepared precursors (SI, SII) are subjected to several heat treatments (SIII–SV). The synthesized nanoparticles are characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The samples are tested as electrocatalyst for oxygen reduction reaction in an alkaline electrolyte. It is shown that the electrocatalytic properties of the synthesized nanoparticles are highly dependent on the heat treatment atmosphere and duration. The heat treatment under ammonia atmosphere at  $1000^\circ\text{C}$  for 10 h (SIV) increased the ORR mass activity from  $-0.64$  (SI) to  $-1.28 \text{ mA mg}^{-1}$  (SIV) at  $-0.6 \text{ V}$  vs. SCE. Moreover, the heat treated sample (SIV) shows almost twice ORR mass activity as commercial TiN. Rotating disk electrode (RDE) measurements exhibit ORR on commercial TiN proceeds via two parallel pathways including two and four electrons, resulting in almost 60%  $\text{H}_2\text{O}_2$  production, while SIV sample improves ORR by reducing  $\text{H}_2\text{O}_2$  formation to almost 16%. The high ORR activity and stability of the sample SIV are mainly due to (i) random layer structure of carbon that combines through a hybrid state with TiN nanoparticles, (ii) unstoichiometric nitrogen and oxygen doped into TiN lattice, and (iii) higher electrochemical surface area. Moreover, the possible pathways of carbon phase formation in vicinity of supercritical reaction are discussed.

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## 1. Introduction

In polymer electrolyte fuel cells (PEFCs) the oxygen reduction reaction (ORR) is one of the important electrocatalytic reactions for energy conversion [1–3]. Noble metal catalysts are required to be replaced with other electrocatalysts for large-scale application of the technology. In this regards, nitride/oxy-nitrides of group IV and V transition metals show high electrocatalytic performance for ORR [1]. Among these catalysts titanium nitride/oxy-nitride has been developed for many electrochemical applications due to its specific properties such as excellent conductivity, inertness, and

good optical reflectivity at long wavelengths [4–7]. On the other hand, titanium nitride/oxy-nitride has been synthesized by various methods. A number of physical, chemical and solid state methods have been reported in the literature for synthesizing the nitride (/oxy-nitride) in new morphologies with high surface areas as well as in the thin film form [8–13]. The most popular approaches for synthesizing the nitride are the direct nitridation of titanium metal and the carbothermal reduction of  $\text{TiO}_2$  [10–12]. Recently, there are focuses on presenting new methods for TiN synthesis with more efficiency, lower cost processes and higher surface area and purity [13–15]. Examples of these methods are mechano-chemical reactions with or without subsequent heat-treatments [15,16], benzene-thermal synthesis [17], reaction under autogenic pressure at elevated temperature technique [18,19], hydrazide sol-gel process [14], sol-xerogel processes followed by pyrolysis under ammonia or nitrogen [20,21], sol-gel route followed by pyrolysis under ammonia at ambient temperature for preparing TiN

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**Table 1**  
Synthesis and heat treatment conditions.

Sample	Synthesis Conditions		Heat Treatment		
	Temperature/°C	Time/h	Atmosphere	Temperature/°C	Time/h
SI	380	1	–	–	–
SII	380	8	–	–	–
SIII	380	1	NH <sub>3</sub>	1000	3
SIV	380	1	NH <sub>3</sub>	1000	10
SV	380	1	N <sub>2</sub>	1000	10

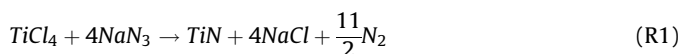
nanocrystalline thin films and nanopowder [21–24], electrochemical synthesis [13,25,26], and supercritical combustion synthesis of TiN [27]. These techniques are extremely attractive in that new morphologies with high surface areas and tailorable pore structures can be produced, which are potentially useful in catalysis, photonic band gap materials, battery electrodes, etc. Among all the mentioned methods, synthesis in supercritical media is a unique one due to adjustability of size, morphology, and crystal structure of the nanoparticles [28]. The most important advantages of supercritical media are faster kinetics, smaller particle size, and ability of tuning the process that is a result of the extreme change of solvent physical properties in the proximity of its critical point [29,30].

Benzene has a well known stable chemical structure with critical temperature of 298 °C. However, Hu et al. [17] suggested the possibility of decomposition of benzene during the synthesis of TiN under supercritical condition. In the present study, we intend benzene to be partially decomposed to form nanocrystalline TiN/C composite because carbon-modified TiN is expected to show higher and more stable ORR activity. Moreover, some heat treatments under ammonia and N<sub>2</sub> atmospheres are applied to as-prepared precursor (SI, see Table 1) because it should have effective role on the powder crystallinity and consequently on the ORR activity. For better understanding of synthesized catalyst nature and justifying their variant ORR activity several analyses are done. X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM) are used to analyze phase evolution and morphology of the powders. The surface structure and chemical state of samples are analyzed using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). These combined techniques gain a comprehension of the molecular processes occurring in the precursor during the reaction in supercritical benzene and its subsequent phase evolution after heat-treatment.

## 2. Experimental

### 2.1. TiN nanoparticles synthesis

TiN nanoparticles were prepared using supercritical benzene environment, by the following reaction:



as described by Hu et al. [17]. All reactions were conducted in an ultra high purity (UHP) N<sub>2</sub> filled glove box. Used chemicals were benzene (C<sub>6</sub>H<sub>6</sub>, Merck, 99.96%) as solvent and carbon source, and titanium tetrachloride (TiCl<sub>4</sub>, Merck, >99%) and sodium azide (NaN<sub>3</sub>, Merck, >99%) as reactants. The reaction was performed in a stainless steel batch reactor which was designed especially to endure working temperature and pressure up to 550 °C and 610 atm, respectively (manufactured by Techno-Pars Co., Iran). The capacity of the reactor was 30 cm<sup>3</sup>, but it was always loaded with one third of its volume in order to keep the sufficient safety margin. In the synthesis procedure, 1.95 g NaN<sub>3</sub>, 0.8 cm<sup>3</sup> TiCl<sub>4</sub> and 10 cm<sup>3</sup> of benzene were put into the

reactor and the temperature was set at 380 °C, meanwhile residence time was changed from 30 min to 8 h. The reactor after being removed from a furnace was quenched, and the obtained nanoparticles were collected, filtered, and washed with 0.1 M hydrochloric acid solution and distilled water. The final product was dried under vacuum at 80 °C for 10 h to obtain a black powder.

### 2.2. Heat-treatments

In order to improve the crystallinity of the as-prepared precursor (SI), it was further heat-treated at 1000 °C for 3–10 h using anhydrous ammonia and UHP nitrogen atmospheres at a heating rate of 5 °C min<sup>-1</sup> up to 800 °C and 1 °C min<sup>-1</sup> up to 1000 °C followed by a constant cooling rate of 5 °C min<sup>-1</sup> to room temperature. Meanwhile, the flow rate of the gas was maintained at 100 cm<sup>3</sup> min<sup>-1</sup>. The samples' given names and their appropriate synthesis conditions are mentioned in Table 1. Moreover, to evaluate the role of carbon inclusion in the synthesized nanoparticles, ORR activity of commercial TiN (Wako, 50 nm) was evaluated for comparison.

### 2.3. Characterization

In order to examine the phase evolution and crystallization behavior, a STOE D-64295 diffractometer (Cu-Kα radiation, λ = 1.54056 Å) was used employing a step size of 0.03. The mean size of crystallite was estimated from the broadening of the XRD lines using Williamson Hall Method. The instrumental errors were corrected using powder diffraction pattern of a silicon sample. The relationship  $\beta_{\text{true}}^2 = \beta_{\text{exp}}^2 - \beta_{\text{inst}}^2$  was used where  $\beta_{\text{exp}}$  and  $\beta_{\text{inst}}$  denotes FWHM of experimental and instrumental patterns, respectively [31]. Fourier transform infrared spectroscopy (FTIR) studies were performed using an Magna-IR™ spectrometer 750. The samples were prepared using a KBr-pellet technique.

Field emission scanning electron microscopy (JSM-7001F) equipped with an energy dispersive spectroscopy (EDS) probe and transmission electron microscopy (JEM-2100) were used to observe the morphology and particle size of as-prepared (SI, SII) and heat treated (SIII, SIV) powders.

XPS analyses were performed by using a ULVAC-PHI 5600 spectrometer with an Al Kα exciting X-ray source. Wide scan, in the binding energy range 1400–0 eV, and high-resolution (Ti2p, N1s, C1s, O1s) spectra were obtained at an electron take-off angle of 45°. The XPS spectra were fitted using a non-linear least squares fit with a Gaussian peak shape and Shirley method was used to subtract the background prior to each fit.

### 2.4. Electrochemical measurements

Electrochemical measurements were conducted in 500 cm<sup>3</sup> of 0.1 M NaOH solution at 298 K using a potentio-stat Ivium CompactStat. A Pt mesh and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. ORR activity was measured by the following procedure: (i) purge the oxygen dissolved in the electrolyte by bubbling Ar for 30 min; (ii) measure the baseline current for ORR by sweeping potential (0.3 → -1.3 → 0.3 V) at 5 mV/s; (iii) saturate the electrolyte with air by bubbling air for 30 min; (iv) evaluate the ORR activity by sweeping potential (0.3 → -1.3 → 0.3 V) at 5 mV/s and various rotation speeds.

Rotating disc electrode (RDE) measurements were performed using GC and Pt electrodes with disc radius of 5 mm. For coating RDE a suspension of 5 mg catalyst in a mixture of 970 μl of isopropanol, 470 μl of distilled water, and 1.1 μl of 5% nafion solution [1] was prepared and appropriate amount was dropped on the disc electrode surface and dried at room temperature in air.

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