

# A Low Temperature Synthetic Route to Nanocrystalline TiN

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## ABSTRACT

A simple chemical synthetic route has been developed to prepare nanocrystalline titanium nitride (TiN) in an autoclave, by the reaction of metallic Ti with NaNH<sub>2</sub> at low temperature of 500–600 °C. The samples were characterized by X-ray powder diffraction, transmission electron microscopy, and X-ray photoelectron spectra. The possible reaction mechanism of this process is also discussed. This method may be extended to the synthesis of other metal nitrides.

## KEYWORDS

Nanocrystalline, titanium nitride, synthesis.

## 1. Introduction

In recent years, great attention has been paid to titanium nitride (TiN) for its excellent physical and chemical properties, such as high chemical stability, hardness (~2160 kg/mm<sup>2</sup>), and high melting point (~3000 °C).<sup>1,2</sup> It is suitable for applications in cutting tools, wear-resistant parts and high temperature materials.<sup>3–5</sup> In addition, its high electronic conductivity ( $5 \times 10^4$  Ω/cm) makes it an important electrically conducting ceramic for use in self heating crucibles or as a conductor for electronic application.<sup>6–8</sup> Besides these, titanium nitride is also an excellent catalyst.<sup>9</sup>

Conventionally, TiN is synthesized with a variety of methods, including self-propagating high-temperature synthesis (SHS), by heating or igniting fine metal powders under high nitrogen pressure at 1200 °C,<sup>10</sup> the reaction of nanosized titania nitrified in flowing ammonia gas,<sup>11,12</sup> and solid state metathesis (SSM) routes.<sup>13</sup> Other methods, such as combustion synthesis,<sup>14</sup> supersonic thermal plasma expansion,<sup>15</sup> electrophoretic deposition<sup>16</sup>, direct current magnetron sputtering<sup>17</sup>, and mechanical milling<sup>18–20</sup> were also reported. A.J. Rebecca and co-workers<sup>21</sup> investigated a metathesis reaction between TiCl<sub>3</sub> and Ca<sub>3</sub>N<sub>2</sub> at 1665 °C. Recently, Hokamoto *et al.*<sup>22</sup> prepared TiN powders through electrical wire explosion of a titanium wire in liquid nitrogen. However, most of these reactions involve temperatures higher than 1000 °C, or complex procedure for extended periods of time<sup>23</sup>. In recent years, autoclaved synthesis of TiN nanomaterials from titanium sources of TiO<sub>2</sub>, TiCl<sub>4</sub> has been developed<sup>24–27</sup>.

In the present work, we describe a simple chemical synthetic route to nanocrystalline TiN at 500–600 °C, using metallic Ti and sodium amide (NaNH<sub>2</sub>) as source materials. The reaction was carried out in an autoclave and the crystals were characterized by X-ray powder diffraction, transmission electron microscopy, and X-ray photoelectron spectra.

## 2. Experimental

### 2.1 Synthesis of TiN

All the manipulations were carried out in a dry glove box with Ar flowing. Typically, the reaction was carried out in a stainless steel autoclave with 50 mL capacity. 0.479 g metal Ti (0.01 mol), 1.56 g NaNH<sub>2</sub> (0.04 mol) (Purchased from Shanghai Chem.

Reagent Co.) were mixed in the autoclave. Then the autoclave was sealed, and maintained at 500, 550 and 600 °C for 12 h in an oven. After being cooled to room temperature, the products were collected and washed with absolute ethanol, dilute hydrochloric acid, and distilled water for several times to remove the impurities. The final products were vacuum-dried at 60 °C for 4 h. Black powder was obtained.

### 2.2. Techniques of Characterization

The obtained samples were characterized by X-ray powder diffraction (XRD) on a Rigaku Dmax-γA X-ray diffractometer with Cu Kα radiation ( $\lambda = 1.54178$  Å). The morphology of nanocrystalline TiN was examined from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg Kα X-rays as the excitation source.

## 3. Results and Discussion

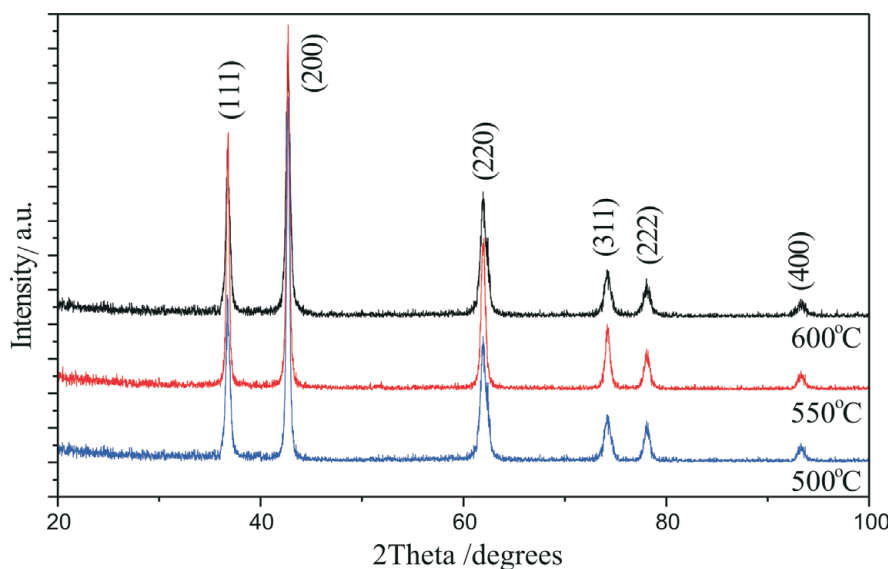
### 3.1. XRD Characterization of the Products

Figure 1 shows the XRD pattern of the samples prepared at 500 °C, 550 °C and 600 °C for 10 h, respectively. In Fig. 1, all of the six diffraction peaks [(111), (200), (220), (311), (222), and (400)] at different d-spacing can be indexed as cubic titanium nitride. The lattice constants are  $a = 4.244$  in good agreement with  $a = 4.241$  (JCPDS card no. 38-1420). No evidence of crystalline Ti, TiO<sub>2</sub> or other impurities is observed.

### 3.2 XPS Characterization of the Samples

The composition information of the TiN sample could be obtained from the XPS spectra, as shown in Fig. 2a. The survey spectrum indicates the presence of Ti and N elements. Small amount of carbon and oxygen were also detected, which may be due to the absorption of oxygen, water, or carbon on the powder surface<sup>24,25</sup>. The Ti2p and N1s core-level regions were examined. In Fig. 2b, the peaks at 458.10 and 464.20 eV, corresponding to the binding energy of Ti2p<sub>3/2</sub>, are close to that in TiN.<sup>28</sup> The detected N1s core-level region (in Fig. 2c) at 397.35 eV is also consistent with the reported value for TiN.<sup>29</sup> Quantification of the peak intensities reveals that the atomic ratio of Ti to N is 1.09:1.00,

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**Figure 1** XRD patterns of the TiN samples.

which agrees well with the chemical stoichiometric relationship between Ti and N.

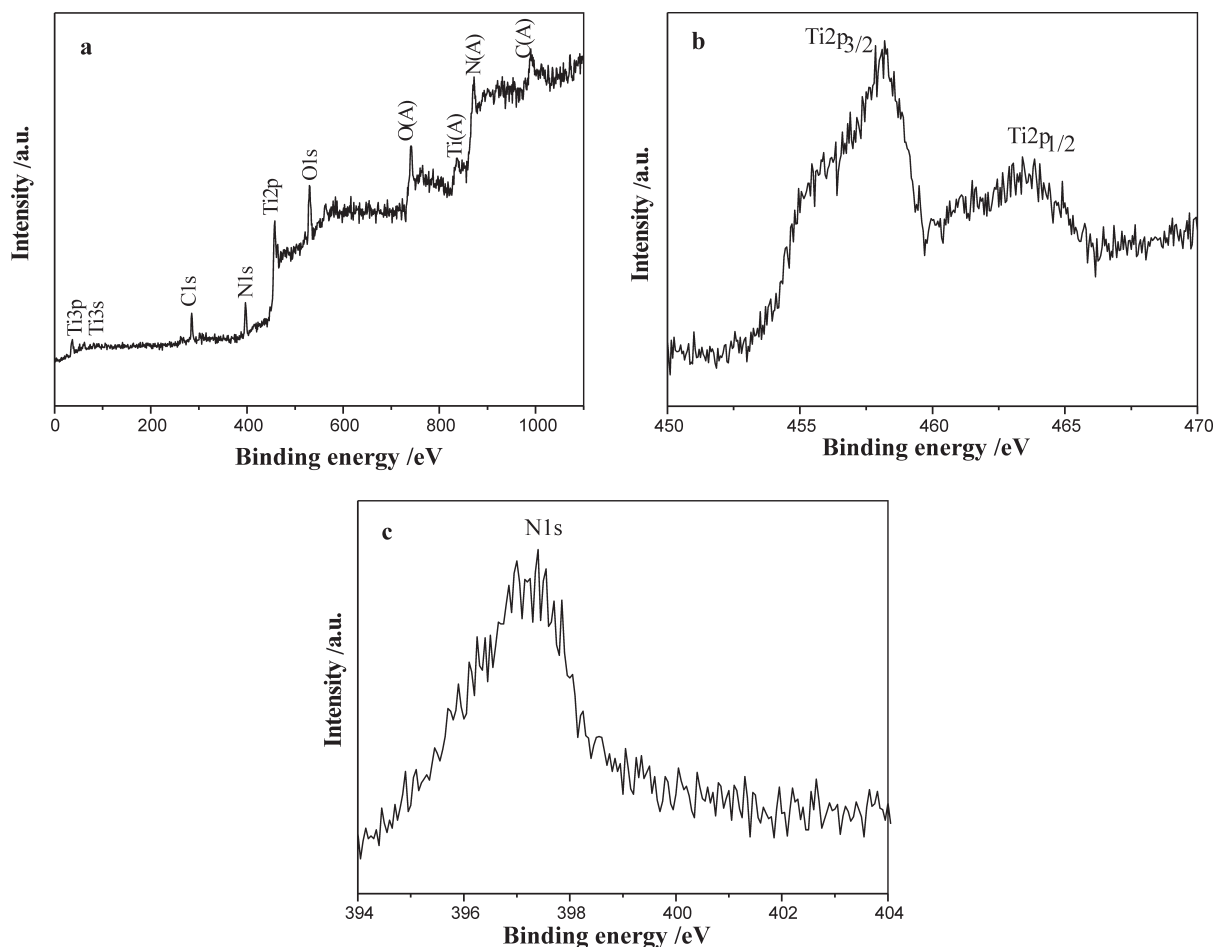
### 3.3. TEM Images of the Products

The morphology of the as-prepared products was investigated by TEM.

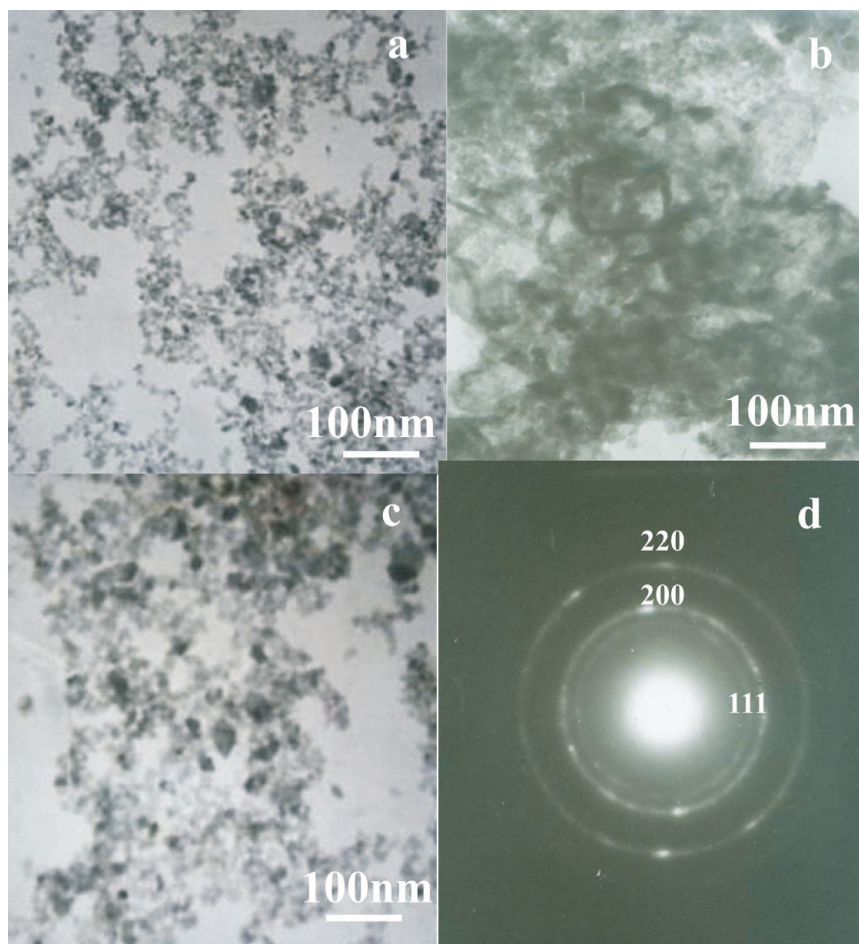
Figure 3 shows the TEM images and selected area transmission electron diffraction (SAED) of the samples, respectively. Figure 3a is the image of TiN nanocrystallites prepared at 500 °C

for 12 h. We can observe that TiN nanocrystallites have particle morphology with uniform diameter about 20–30 nm.

It was found that a suitable reaction temperature is a key factor in the formation of TiN. An optimum reaction temperature for the nanocrystalline TiN was about 500–600 °C. If the temperature was lower than 450 °C, the yield of TiN was low (Fig. 3b). When the temperature was higher than 500 °C, the crystallinity of TiN increased evidently (as shown in Figs. 3a and 3c). Varying the treatment time between 10 and 24 h at 500–600 °C did not



**Figure 2** XPS spectra of the nanocrystalline TiN sample: (a) Survey spectra; (b) Ti2p region; and (c) N1s region.



**Figure 3** TEM images of as-prepared TiN nanocrystallites prepared at (a) 500 °C, (b) 450 °C, (c) 600 °C, and (d) SAED pattern of the TiN nanocrystallite.

significantly affect the crystallinity or the yield of TiN, indicating a rapid reaction between Ti and  $\text{NaNH}_2$  once the reaction is initiated. SAED pattern obtained from the single nanocrystallite is also shown in Fig. 3d, the three polycrystalline rings in accordance with TiN [(111), (200) and (220)] confirm the XRD result.

### 3.4. Feature of Present Study

It is well-known that choosing reactive sources is the vital factor to a novel synthetic routes. A previous report on  $\text{NaNH}_2$  indicated that elemental Na,  $\text{N}_2$ , and  $\text{H}_2$  can be generated from the decomposition of  $\text{NaNH}_2$  when the temperature is higher than 330 °C<sup>30</sup> (reaction 1) and Ti is rather reactive toward nitrogen at elevated temperatures, and an irreversible reaction between Ti and  $\text{N}_2$  can easily occur<sup>31</sup> (reaction 2). Furthermore, the newly formed  $\text{H}_2$  would also react with  $\text{NaNH}_2$  on this condition (reaction 3). This results in a transient intermediate NaH and the gases  $\text{NH}_3$  and  $\text{H}_2$  (reactions 3 and 4), which is favourable to the formation and crystallization of TiN. The layer of  $\text{TiO}_2$  that invariably coats Ti-metal is then removed by the liquid sodium to expose the reactive metal surface, resulting in the above reactions. Therefore it is reasonable to consider a decomposition-nitridation route to the formation process of TiN. The overall reactions might be illustrated as follows:



One feature of the present study is carrying out the reaction in an autoclave, which is inspired by the previous reports,<sup>32,33</sup> and two factors may play key roles in the present study. Firstly, the byproduct, molten Na, plays a role of reaction-medium to control the reaction rate and particle size;<sup>34</sup> additionally it can absorb the reaction enthalpy released from this process and maintain a relative low reaction temperature.<sup>35</sup> In addition, the release of  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$  rapidly increases the pressure in the system, which may also be helpful to the formation of TiN nanocrystallites.<sup>36</sup>

### 4. Conclusions

In summary, nanocrystalline TiN have been synthesized by the reaction of Ti and  $\text{NaNH}_2$  at the temperature of 500–600 °C for 12 h in an autoclave. XRD pattern reveals the synthesized TiN crystallized in cubic crystal structure. The TEM image shows particle morphology crystalline with uniform diameter of about 20–30 nm. An atomic ratio of N to Ti of 1.09:1.0 was determined from X-ray photoelectron spectra. We believe this work might pave the way for the synthesis of other metal nitrides.

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