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Synthesis and characterization of titanium nitride nanoparticles

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ABSTRACT

Titanium nitride (TiN) materials have gained an interest over the past years due to their unique characteristics, such as thermal stability, extreme hardness, low production cost, and comparable optical properties to gold. In the present study, TiN nanoparticles were synthesized via a thermal benzene route to obtain black nanoparticles. Scanning electron microscopy (SEM) was carried out to examine the morphology. Further microscopic characterization was done where the final product was drop cast onto double-sided conductive carbon tape and sputter-coated with gold/palladium at a thickness of 4 nm for characterization by field emission scanning electron microscopy (FE-SEM) with energy dispersive X-Ray spectroscopy (EDS) that revealed they are spherical. ImageJ software was used to measure the average size of the particles to be 79 nm in diameter. EDS was used to determine the elements present in the sample and concluded that there were no impurities. Further characterization by Fourier Transform infrared (FTIR) spectroscopy was carried out to identify the characteristic peaks of TiN. X-ray diffraction (XRD) revealed typical peaks of cubic phase titanium nitride, and crystallite size was determined to be 14 nm using the Debye-Scherrer method. Dynamic light scattering (DLS) analysis revealed the size distribution of the TiN nanoparticles, with nanoparticles averaging at 154 nm in diameter. Zeta potential concluded the surface of the TiN nanoparticles is negatively charged.

Keywords: Titanium Nitride Nanoparticles, Synthesis, Characterization, Biocompatibility.

1. INTRODUCTION

Nanomaterials have captivated the attention of many in the past few decades due to their significant difference in properties from their bulk counterparts [1]. Titanium nitride is a hard ceramic material used mainly as a coating with other materials to enhance their properties [2]. TiN possesses remarkable properties such as high melting point [3], high electron conductivity [4], mechanical hardness [5], low cost [6], and corrosion resistance [7]. Titanium nitride has generated an interest in a wide range of applications in the fields of biology [8] and microelectronics [9]. This material has been studied for the use of coatings on biomedical implants where layers of TiN do not cause cellular damage when tested on cell lines [10].

Numerous methods used for the synthesis of titanium nitride nanoparticles include combustion reactions [11], solid-state metathesis (SSM) [12], chemical reduction [13], and a few others. Synthesis of TiN nanoparticles, however, requires high temperatures with equipment that is not always readily available. In relation to this research, Luyang Chen and group have synthesized TiN hollow

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spheres at room temperature [14]. Similarly, Hu and group synthesized TiN nanoparticles at lower temperatures than other groups [15].

In this study, a benzene-thermal route approach was utilized to synthesize titanium nitride (TiN) nanoparticles. Characterization methods such as Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction Spectroscopy (XRD), and Dynamic Light Scattering (DLS) were used to analyze the properties of the titanium nitride nanoparticles.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

Titanium nitride nanoparticles were synthesized via a benzene-thermal route at low temperatures. All manipulations were performed in a glovebox with constant nitrogen gas flow. Sodium azide (NaN_3) was weighed using an analytical scale to obtain 7.0001 g and placed in a 50 ml capacity Erlenmeyer flask. A syringe was used to extract 40 ml of benzene which was added to the flask containing the sodium azide. Another syringe was used to obtain 3 ml of titanium chloride ($TiCl_4$), ensuring that the process of pouring the $TiCl_4$ into the benzene solution was fast. The mixture was placed inside a furnace (Thermolyne FB1310 M), and the temperature was set to 350 °C for 6 hours. The precipitate was then collected and washed with 0.1 M HCl solution three times using a centrifuge for 15 minutes at 5,000 rpm. The material was washed and centrifuged three more times with deionized water for 15 minutes at 5,000 rpm. The final product was placed in a petri dish and dried under a vacuum at 80 °C for 1 hour.

2.2. Characterization

2.2.1. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) was carried out using PHENOM ProX with EDS attachment (Phenom, FEI Company, Hillsboro, OR, USA). A suspension was prepared of synthesized TiN in deionized water and sonicated for 5 minutes. An SEM pin mount was prepared by attaching double-sided conductive carbon tape, and 10 μl of the prepared suspension was pipetted on the other end. The SEM pin mount was left to dry overnight. The sample was run with an accelerating voltage of 15 kV to obtain the approximate size and shape of the TiN nanoparticles. EDS was used for elemental analysis of the synthesized TiN nanoparticles.

2.2.2. Field Emission Electron Microscopy

Further characterization was performed by field emission electron microscopy (FE-SEM) using Hitachi S-4700 Field Emission Scanning Electron Microscope (Hitachi, Chiyoda, Tokyo, Japan). To prepare the sample, a suspension of synthesized TiN nanoparticles in ethanol was sonicated for two hours for uniform dispersion, drop-cast onto double-sided carbon tape, and dried overnight. The material was then sputter-coated with gold/palladium at a thickness of 4 nm and loaded into the equipment for FESEM analysis. The capacity of FESEM to generate clearer images at higher magnifications and better resolution allows the user to see more details in the morphology than SEM [16].

2.2.3. Fourier Transform Infrared Spectroscopy

Characterization by FTIR is used as a method that generates a spectrum that contains absorption peaks unique to a material [17]. In this study, Agilent Cary 630 Fourier Transform—Infrared Spectrometer (FTIR) (Agilent, Santa Clara, CA, USA) was used to identify functional groups in the synthesized TiN sample. The parameters were set to transmittance mode in the range of 4000 cm^{-1} to 650 cm^{-1}. Preparation involved using a small amount of dry TiN nanoparticles sample on the crystal and pressing down to collect the data.

2.2.4. X-Ray Diffraction

The material was further characterized by X-ray spectroscopy (XRD) using the PANalytical Empyrean Series 2 (Malvern Panalyrical, Malvern, United Kingdom) X-Ray Diffraction System. XRD is used to determine the crystal structure and space group of the phases of the sample [18]. The sample was prepared by adding TiN nanoparticles on a glass plate and pressing it down prior to placing it on the XRD machine. XRD patterns were recorded and analyzed using X-rays from Cu Kα (1.541 Å).

2.2.5. Dynamic Light Scattering

Dynamic light scattering (DLS) is a method utilized to determine the size distribution of particles in a suspension or solution based on the Brownian motion of the particles [19]. DLS was performed to obtain the average size of the synthesized TiN nanoparticles. Zeta potential was also determined, revealing the particles' surface charge. Sample preparation consists of suspending the sample in ethanol and placing the cuvette in the instrument.

3. RESULTS AND DISCUSSION

3.1. Synthesis

The titanium nitride nanoparticles were synthesized successfully using a low-temperature approach where a black powder was obtained containing the nanoparticles. This low-temperature approach is effectively more simple and requires less equipment compared to traditional synthesis methods [20].

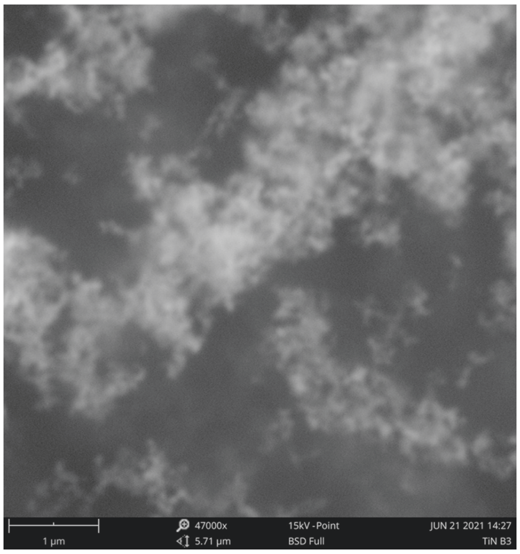

Fig. 1. SEM image representing titanium nitride nanoparticles at 47000X.

3.2. Characterization

Titanium nitride nanoparticles were synthesized via a benzene route at low temperatures and characterized by several methods, including SEM, EDS, FESEM, FTIR, XRD, and DLS. The results of these methods are discussed below.

3.2.1. SEM—EDS Analysis

SEM analysis was performed to obtain the surface composition of the sample. The TiN nanoparticles in Figure 1 were observed to be agglomerated and of nanometer size. Image J software was used to get an approximate size of the nanoparticles ranging from 50 nm to 150 nm. Figure 2 shows EDS analysis with elements present in the sample: carbon, nitrogen, titanium, and oxygen.

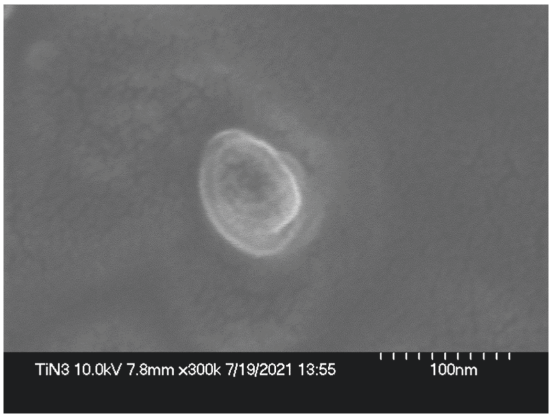

Fig. 3. FESEM image of titanium nitride nanoparticles on carbon tape sputter coated with gold/palladium at a thickness of 4 nm at 300,000X.

3.2.2. FESEM

A higher-resolution image of the TiN nanoparticles was obtained by FESEM in Figure 3. Sputter coating of the sample allows for higher magnification and, thus, more detail on the morphology. With this method, single particles can be seen; in this case, the nanoparticles are spherical and around 50 nm in size.

3.2.3. FTIR Analysis

Figure 4 is the Fourier transform infrared spectra generated from 650–4000 cm^{-1}. According to Snyder and group, a single broad peak is observed at 670 cm^{-1} associated with the formation of titanium nitride [21].

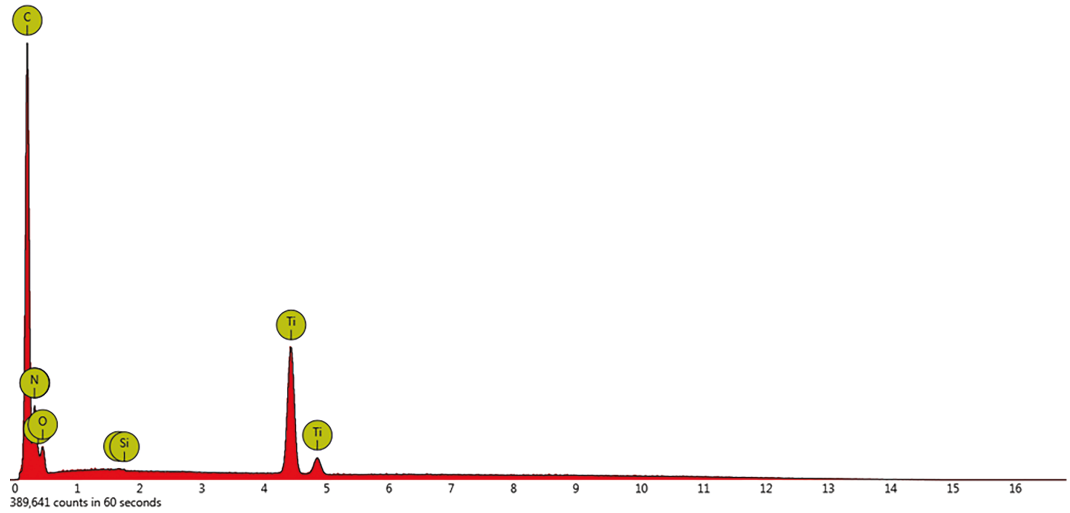

Fig. 2. EDS spectra of TiN nanoparticles with absorption peaks corresponding to carbon, nitrogen, oxygen, titanium, and silicon. The high concentration of carbon can be attributed to the carbon tape substrate.

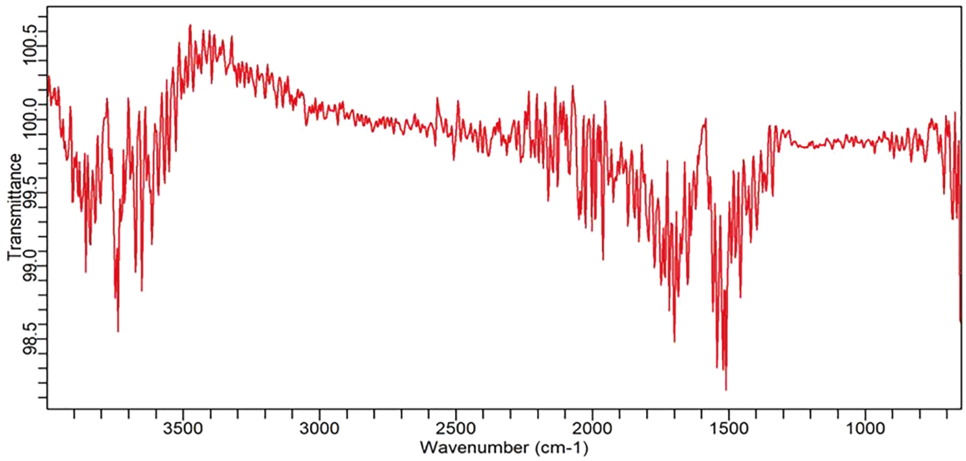

Fig. 4. FTIR transmission spectra of titanium nitride nanoparticles.

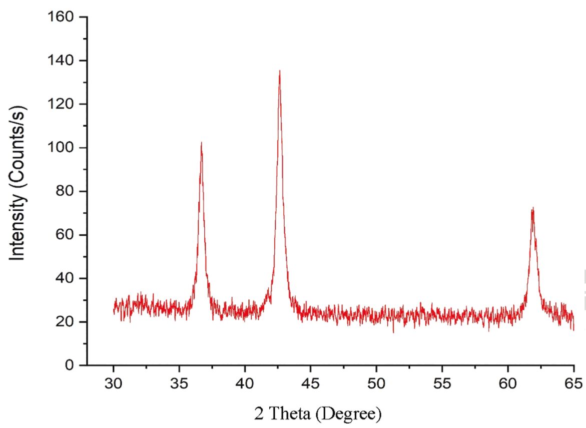

Fig. 5. XRD diffraction pattern of TiN nanoparticles. Given peaks coincided with literature for cubic phase titanium nitride with peaks observed at 36.6°, 42.5°, and 61.7°.

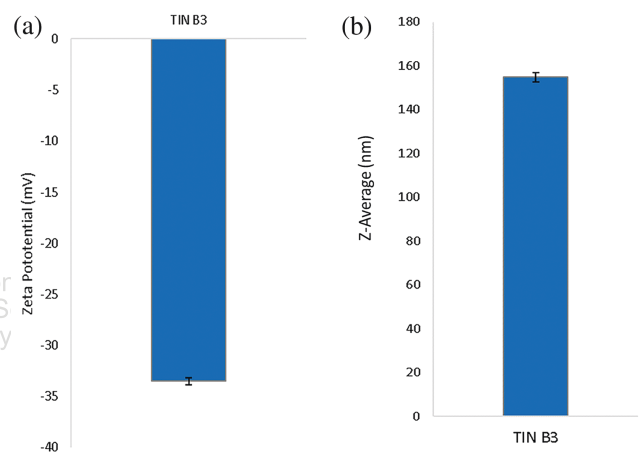

Fig. 7. (a) Z-average histogram of TiN nanoparticles reveals average size is 154 nm. (b) Zeta potential reveals surface charge of TiN nanoparticles is highly electronegative.

3.2.4. XRD Analysis

Figure 5 shows the XRD patterns of the TiN nanoparticles sample. The peaks at 36.6°, 42.5°, and 61.7° represent diffraction peaks corresponding to the crystal planes (1,1,1), (0,0,2), and (0,2,2), respectively. Peaks were confirmed by referring to the ICDD PDF card 65-0715 [22]. No other phases were present, confirming pure titanium nitride with no impurities. Crystallite size was determined to be 14 nm by the Debye-Scherrer method.

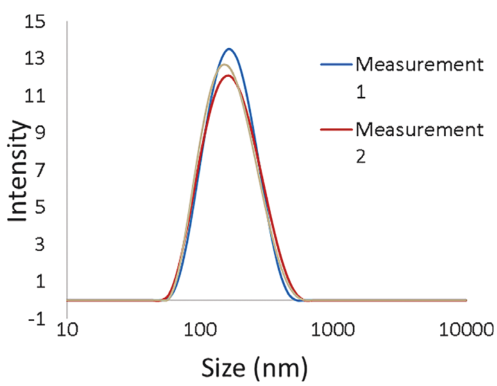

Fig. 6. DLS measurement of TiN nanoparticles with size distribution curves.

3.2.5. Dynamic Light Scattering Analysis

Dynamic light scattering was performed to get the mean size of the synthesized TiN particles. The size distribution curves are shown in Figure 6. The Z-average shown in Figure 7(a) reveals the mean size of the nanoparticles being 154 nm. Figure 7(b) represents the Zeta potential of the nanoparticles where the surface charge is found to be highly negative.

4. CONCLUSIONS

In conclusion, this study discussed the synthesis method for the synthesis of titanium nitride nanoparticles and discussed various characterization studies. The titanium nitride nanoparticles were successfully synthesized via a thermal benzene route, where black nanoparticles were obtained. The synthesized nanoparticles were characterized by SEM, EDS, FESEM, FTIR, XRD, and DLS analysis. SEM and FESEM revealed the titanium nitride nanoparticles to be spherical and in the nanometer range, with the smallest nanoparticles around 50 nm. EDX analysis ensured the elemental composition of the material and determined there were no impurities. FTIR spectra revealed characteristic peaks of titanium nitride. XRD determined the crystal structure of the nanoparticles, crystallite size, and further confirmed the synthesis of titanium nitride nanoparticles. DLS analysis determined the average size of the nanoparticles to be around 154 nm. Zeta potential revealed the material is negatively charged.

Conflicts of Interest

The authors declare no conflicts of interest.

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