ISSN: 2754-4966

Journal of Nanosciences Research & Reports

SCIENTIFIC Research and Community

Research Article

Open Access

TiN Nanoparticles for Biosensing Applications

Nicole M Nazario Bayon[1,2], Paula Fortuno[1], David Keene[1], Nithin Krisshna Gunasekaran[1,2], Natalia Noginova[1], Krishnan Prabhakaran[2] and Govindarajan T Ramesh[1,2*]

[1]Center for Materials Research, Norfolk State University, 555 Park Avenue, Norfolk, VA, 23504, USA
[2]Department of Biology, Norfolk State University, 700 Park Avenue, Norfolk, VA, 23504, USA

ABSTRACT

Titanium nitride (TiN) is a refractory material that possesses optical properties often compared to gold. In this study, we fabricate and study plasmonic TiN nanoparticles for potential use in biosensing applications. TiN nanoparticles of an average diameter of 154 nm are fabricated with chemical synthesis methods and then exposed to a pulsed laser illumination for 40 minutes. Exposure to laser radiation induced a color change from grey to blue associated with laser-induced breaking of large polycrystalline particles into smaller ones. UV-VIS transmission spectrum of the irradiated sample shows a well-defined dip at 635 nm, associated with surface plasmon resonance. Using various solvents, we demonstrate that the position of the dip is sensitive to the solvent, which presents interest for biosensing applications using TiN nanoparticles.

Corresponding author

Govindarajan T Ramesh, Center for Materials Research, Norfolk State University, 555 Park Avenue, Norfolk, VA, 23504, USA.

Received: June 26, 2024; **Accepted:** July 01, 2024; **Published:** July 07, 2024

Keywords: Titanium Nitride, Laser Radiation, UV-Vis, Surface Plasmon Resonance, Biosensing

Introduction

Plasmonic and metamaterials have introduced a remarkable research interest over the last two decades. The possibility of concentrating and controlling the electromagnetic field on the subwavelength scale brings extraordinary control of light, strong enhancement of linear and nonlinear optical processes, and new applications such as nano-scale optical interconnects, optical cloaking, and super-resolution imaging [1-3]. However, the practical applications are still limited due to the significant loss in, and the excessive large in magnitude real parts of the metal permittivity [3-5].

Titanium nitride (TiN) is considered to be a promising material since it could overcome some of the problems above [6, 7]. Even though the optical losses in metal nitrides such as TiN are not smaller than those of noble metals, the magnitude of the actual permittivity of these materials in the visible range is substantially lower than that of noble metals due to low carrier concentration. In addition, unlike noble metals, these metal nitrides' optical characteristics can be adjusted by merely altering the processing conditions [8]. Gururaj et al. demonstrated that in the visible and near-IR frequencies, titanium nitride can be used as an alternative plasmonic material for plasmonic and metamaterial applications and showed that titanium nitride exhibits process-dependent characteristics while being a non-stoichiometric material [3]. In addition, a comparison of TiN and traditional plasmonic materials revealed that TiN exhibits equivalent performance in plasmonic applications and noticeably superior performance in metamaterial devices, such as hyperbolic meta-material devices and transformation optics. By employing dielectric gratings for inducing surface plasmon polaritons (SPPs) on TiN/dielectric interfaces, titanium nitride was demonstrated to support SPPs in the near-IR range [3].

Manipulations in the size and shapes by simply changing the processing conditions of these nanoparticles allow for the tuning of optical properties [9]. The surface plasmons produced are extremely sensitive to their environment. This allows these plasmonic materials to be used in sensing applications and optical devices [10, 11]. Gold is one of the common materials used for plasmonic applications, which is typically compared to TiN due to the similarity in their optical properties. However, gold has its limitations such as a lower melting point than TiN, and is not compatible with semiconductor technology as it reacts with silicon [12, 13].

The surface plasmon resonance (SPR) of TiN nanoparticles can be observed in the near-infrared range (NIR) within the biological transparency window (650 – 1350 nm), making the nanoparticles a promising material for biomedical applications [14]. Guler et al. used TiN nanoparticles as a local heat source in the NIR and observed that when the TiN nanoparticles were illuminated with laser light the temperature increased at the nanoparticle array [15]. This same local heating mechanism has been investigated for use in cancer therapy. Light-activated heating nanoparticles can be introduced to tumor areas where the nanoparticles are activated via low-intensity laser illumination heating and destroying specific cancerous tissue while not affecting healthy tissue [16]. He et al. used titanium nitride nanoparticles as absorbing agents for plasmon-mediated photothermal therapy (PPT) where they conjugated PEG onto the surface of the nanoparticles and delivered them to a specialized tumor region that was heated via laser illumination and visualized by photoacoustic tomography (PAT) [17]. A more recent application for TiN is sensors. Kaur et al. have designed a titanium nitride-coated PCF-SPR (photonic crystal fiber surface plasmon resonance) sensor that can be used to detect various chemical and biochemical liquids by a shift in the resonance wavelength [18]. Titanium nitride is also a great

candidate for thermophotovoltaics. Common single-junction cells exhibit an efficiency limit of 33.7%, while multi-junction solar cells can absorb different wavelengths of sunlight, thus increasing their efficiency limit to 44.7% [19, 20]. Introducing other plasmonic metamaterial absorbers, such as gold and silver, increases the absorption of different wavelengths of sunlight, bringing their theoretical efficiency limit to 85% [21]. Li et al. have fabricated a TiN broadband absorber capable of absorbing 95% over the range of 400-800 nm [21]. Neuman et al. demonstrated that when particles are suspended in water at room temperature, energy is predominantly focused on vaporizing the water to create steam, with a much smaller fraction resulting in the heating of the fluid [22].

Titanium nitride nanoparticles can be synthesized using various methods such as combustion reactions, solid-state metathesis, and chemical reductions [23-25]. These methods require high-temperature synthesis and long process times. Combustion reactions involve compressing titanium metal powders using a hydraulic press and igniting the sample in an enclosed nitrogen-rich environment [26]. The solid-state metathesis route has demonstrated success in synthesizing TiN powders, but because of high temperatures and long processing times results in grain growth [27]. Yuan et al. synthesized TiN nanopowders using a sodium reduction using TiCl4 and sodium in an environment filled with ammonia gas resulting in an extraction process of over 40 hours [25]. In related research, Luyang Chen et al. have synthesized TiN hollow spheres at room temperature [28]. Likewise, Hu et al. synthesized TiN nanoparticles at lower temperatures than other groups [27].

In this paper, we explore the possibility of modifying the properties of TiN nanoparticles by exposure to intense laser radiation and demonstrate the sensitivity of plasmonic properties in irradiated samples to the local surroundings, which presents interest for future biosensing applications.

Materials and Methods

Experimental

Spherical titanium nitride nanoparticles are synthesized using a benzene thermal method [29]. Characterization with Scanning Electron Microscopy (SEM) shows that the obtained nanoparticles have irregular shapes and an average diameter of 154 nm.

A suspension of TiN nanoparticles in deionized (DI) water is prepared at a concentration of 250 µg/mL. The suspension is placed in an optical cuvette (window dimensions of 10 x 35 mm) and exposed to pulsed laser illumination for 40 minutes. We use an Nd: YAG laser at the wavelength of λ=1064 nm, with a pulse duration of tpulse, ≈ 10 ns, at a 10 Hz repetition rate. The laser pulse energy is 0.9 mJ. The diameter of the spot is 0.86 mm.

UV-VIS spectrophotometry is performed on the TiN nanoparticle suspension before and after exposure. Irradiated and original (non-exposed) suspensions are used to prepare additional samples with different degrees of dilution, and different solvents (water-ethanol mixture).

Results and Discussion

Effect of the Exposure to Intense Laser Light

The TiN nanoparticle suspension exposed to laser radiation shows a significant color change from dark grey to blue as seen in Figure 1. Note that similar behavior was observed with gold nanoparticles: the suspension changed color after exposure to high-intensity pulsed laser light. This has been ascribed to the breaking of particle clusters by light to individual particles, which have the SPR at different ranges [30]. We believe that this process takes place in our case as well. The original TiN samples prepared by chemical methods contain TiN clusters, which can be broken into smaller particles by strong laser pulses.

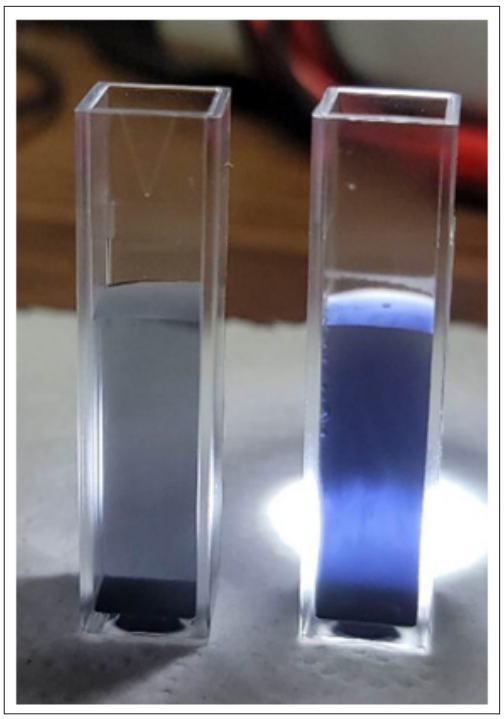

Figure 1: Non-Exposed (left) and Irradiated (right) TiN NPs in DI Water.

This is confirmed by the transmission spectra obtained for non-exposed and irradiated TiN nanoparticles, Figure 2 represents the UV-VIS transmission spectra of the TiN nanoparticles sample (250 µg/mL) and irradiated TiN nanoparticles sample (250 µg/mL). As one can see, the exposed sample transmits at the blue and has a broad minimum of around ~600 nm, while the original suspension has decreased transmission everywhere resulting in grey coloration.

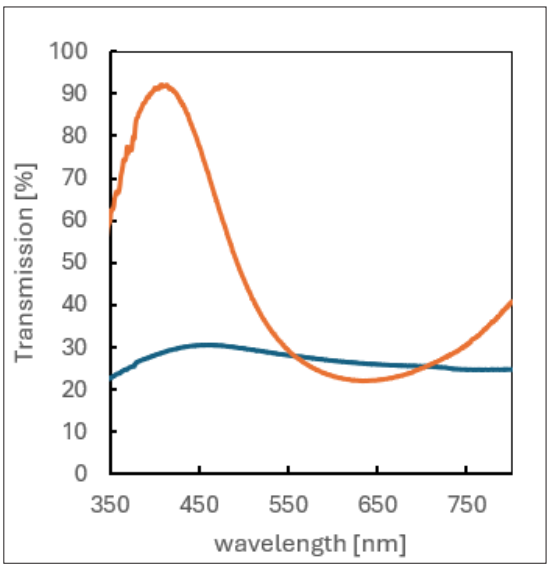

Figure 2: UV-VIS Spectra of TiN Nanoparticles Sample at a Concentration of 250 µg/mL Before (blue) and After (red) Laser

Exposure.

The minimum of the transmission observed in the exposed sample can be accredited to the surface plasmon resonance of the individual small TiN nanoparticles. Note that our samples shown in Figure 2 have high concentrations, and particles are likely of different shapes and sizes; this results in a broad feature instead of a well-defined SPR.

The spectral position of SPR is expected to be sensitive to the environment. In order to explore this, we dilute the original and exposed samples in a water and water-ethanol mixture. Figure 3 shows the UV-VIS transmission spectra of diluted samples of original and irradiated TiN nanoparticles diluted in deionized water and in water/ethanol mixture at concentrations of 75 µg/mL The transmission spectra for the suspension original particles are practically the same in water and water-ethanol mixture. However, they are different for the exposed particles. The resonant dip in diluted irradiated TiN nanoparticles in water is observed around 642 nm and at 650 nm for irradiated TiN nanoparticles in water/ethanol solution.

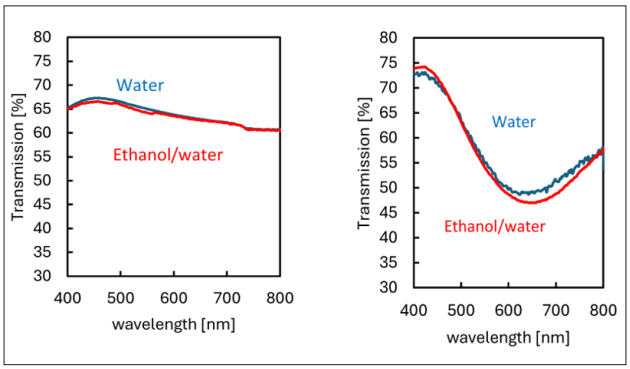

Figure 3: UV-VIS Spectra of (a) Original and (b) Exposed TiN Nanoparticles Sample in DI Water (blue) and DI Water/Ethanol (red). TiN Nanoparticles Concentration is 75 µg/mL.

Conclusion

In our work, we show that the exposure of the TiN synthesized by the chemical synthesis method to the strong laser light radiation is highly beneficial. The laser ablation breaks the clusters, and results in better plasmonic properties of the TiN nanoparticles, which show a well-defined SPR after the exposure. The spectral position of the SPR-related dip in transmission is sensitive to the surrounding medium making this material promising for sensing applications.

Acknowledgment

This work was supported by the National Science Foundation (NSF) CREST # 2112595.

References

1. Berweger S, Atkin JM, Xu XG, Olmon RL, Raschke MB (2011) Femtosecond nanofocusing with full optical waveform control. Nano letters 11: 4309-4313.
2. Barnes WL, Dereux A, Ebbesen TW (2003) Surface plasmon subwavelength optics. Nature 424: 824-830.
3. Naik GV, Schroeder JL, Ni X, Kildishev AV, Sands TD, et al. (2012) Titanium nitride as a plasmonic material for visible and near-infrared wavelengths. Optical Materials Express 2: 478-489.
4. Johnson PB, Christy RW (1972) Optical constants of the noble metals. Physical review B 6: 4370.
5. Kildishev AV, Shalaev VM (2008) Engineering space for light via transformation optics. Optics Letters 33: 43-45.
6. Briggs JA, Naik GV, Zhao Y, Petach TA, Sahasrabuddhe K, et al. (2017) Temperature-dependent optical properties of titanium nitride. Applied Physics Letters 110: 101901.
7. Gadalla MN, Chaudhary K, Zgrabik CM, Capasso F, Hu EL (2020) Imaging of surface plasmon polaritons in low-loss highly metallic titanium nitride thin films in visible and infrared regimes. Optics express 28: 14536-14546.
8. Naik GV, Kim J, Boltasseva A (2011) Oxides and nitrides as alternative plasmonic materials in the optical range. Optical Materials Express 1: 1090-1099.
9. Tathfif I, Rashid KS, Yaseer AA, Sagor RH (2021) Alternative material titanium nitride based refractive index sensor embedded with defects: An emerging solution in sensing arena. Results in Physics 29: 104795.
10. Dolci M, Bryche JF, Leuvrey C, Zafeiratos S, Gree S, et al. (2018) Robust clicked assembly based on iron oxide nanoparticles for a new type of SPR biosensor. Journal of Materials Chemistry C 6: 9102-9110.
11. Salamin Y, Ma P, Baeuerle B, Emboras A, Fedoryshyn Y, et al. (2018) 100 GHz plasmonic photodetector. ACS photonics 5: 3291-3297.
12. Guo WP, Mishra R, Cheng CW, Wu BH, Chen LJ, et al. (2019) Titanium nitride epitaxial films as a plasmonic material platform: alternative to gold. ACS Photonics 6: 1848-1854.
13. Poate JM (1981) Diffusion and reactions in gold films: A review of fundamental aspects. Gold Bulletin 14: 2-11.
14. Schramke KS, Qin Y, Held JT, Mkhoyan KA, Kortshagen UR (2018) Nonthermal plasma synthesis of titanium nitride nanocrystals with plasmon resonances at near-infrared wavelengths relevant to photothermal therapy. ACS Applied Nano Materials 1: 2869-2876.
15. Guler U, Ndukaife JC, Naik GV, Nnanna AA, Kildishev AV, et al. (2013) Local heating with titanium nitride nanoparticles. Proceedings of 2013 Conference on Lasers and Electro-Optics (CLEO) 9-14.
16. Jaque D, Maestro LM, del Rosal B, Haro-Gonzalez P, Benayas A, et al. (2014) Nanoparticles for photothermal therapies. Nanoscale 6: 9494-9530.
17. He W, Ai K, Jiang C, Li Y, Song X, et al. (2017) Plasmonic titanium nitride nanoparticles for in vivo photoacoustic tomography imaging and photothermal cancer therapy. Biomaterials 132: 37-47.
18. Kaur V, Singh S (2019) Design of titanium nitride coated PCF-SPR sensor for liquid sensing applications. Optical Fiber Technology 48: 159-164.
19. Russell TC, Saive R, Augusto A, Bowden SG, Atwater HA (2017) The Influence of spectral albedo on bifacial solar cells: A theoretical and experimental study. IEEE Journal of Photovoltaics 7: 1611-1618.
20. Green M, Dunlop E, Hohl Ebinger J, Yoshita M, Kopidakis N, et al. (2021) Solar cell efficiency tables (version 57). Progress in photovoltaics: Research and Applications 29: 3-15.
21. Li W, Guler U, Kinsey N, Naik GV, Boltasseva A, et al. (2014) Refractory plasmonics with titanium nitride: broadband metamaterial absorber. Adv Mater 26: 7959-7965.
22. Neumann O, Urban AS, Day J, Lal S, Nordlander P, et al. (2013) Solar vapor generation enabled by nanoparticles. ACS Nano 7: 42-49.
23. Vaidhyanathan B, Agrawal DK, Roy R (2000) Novel synthesis of nitride powders by microwave-assisted combustion. Journal of Materials Research 15: 974-981.
24. Gillan EG, Kaner RB (1994) Rapid solid-state synthesis of refractory nitrides. Inorganic chemistry 33: 5693-5700.
25. Yuan B, Yang M, Zhu H (2009) Titanium Nitride Nanopowders

produced via sodium Reductionin Liquid Ammonia. Journal of Materials Research 24: 448-451.

26. Eslamloo Grami M, Munir ZA (1990) Effect of porosity on the combustion synthesis of titanium nitride. Journal of the American Ceramic Society 73: 1235-1239.
27. Hu J, Lu Q, Tang K, Yu S, Qian Y, et al. (2000) Low-Temperature Synthesis of Nanocrystalline Titanium Nitride via a Benzene–Thermal Route. Journal of the American Ceramic Society 83: 430-432.
28. Chen L, Gu Y, Shi L, Ma J, Yang Z, et al. (2004) A room-temperature synthesis of titanium nitride hollow spheres. Journal of Nanoscience and Nanotechnology 4: 896-898.
29. Bayon NN, Gunasekaran NK, Tumkur PP, Lamani BR, Koehne JE, et al. (2022) Synthesis and characterization of titanium nitride nanoparticles. Materials Express 12: 1211-1215.
30. Noginov MA, Zhu G, Gavrilenko VI (2007) Sensitized nonlinear emission of gold nanoparticles. Optics Express 15: 15648-15655.