

A FACILE ROUTE PREPARATION OF ANATASE TiO₂ NANOPARTICLE FOR ENHANCING CUTTING PERFORMANCE OF AISI 304 STAINLESS STEELS

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ARTICLE INFO	ABSTRACT
Received: 04/9/2024	In this study, anatase-phase titanium dioxide (TiO ₂) nanoparticles were synthesized using a straightforward electrochemical method, enhanced by applying of ultrasound waves. Various characterization measurement methods, such as X-ray diffraction, scanning electron microscopy, and Raman spectroscopy, were employed to examine the structural, morphological, and optical properties of the synthesized TiO ₂ nanoparticles. The results indicated that the TiO ₂ nanoparticles exhibited a uniform, sphere-like morphology, moreover a notable reduction in particle size related to the ultrasound assistance. X-ray diffraction and Raman spectra provided further insight into the crystallographic and vibrational characteristics of the TiO ₂ nanoparticles, confirming the presence of a highly crystalline anatase phase. The Raman spectra specifically highlighted the phonon vibrational modes corresponding to the E _g , B _{1g} , and A _{1g} modes, which are characteristic of the anatase phase, demonstrating the improved crystallinity achieved through the ultrasound-assisted method. In addition, when these anatase TiO ₂ nanoparticles were incorporated into lubricating oil, the cutting performance of AISI stainless steel was significantly improved. This enhancement underscores the potential of ultrasound-assisted TiO ₂ nanoparticles synthesis in developing advanced, high-performance lubricating systems.
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TiO ₂ nanoparticle	
Anatase phase	
Electrochemical	
Ultrasound assisted	
Lubricant	

MỘT PHƯƠNG PHÁP ĐƠN GIẢN CHẾ TẠO HẠT NANO ANATASE TiO₂ ĐỂ NÂNG CAO HIỆU SUẤT CẮT THÉP KHÔNG GỈ AISI 304

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THÔNG TIN BÀI BÁO	TÓM TẮT
Ngày nhận bài: 04/9/2024	Trong nghiên cứu này, các hạt nano titan dioxide (TiO ₂) pha anatase được tổng hợp bằng phương pháp điện hóa đơn giản dưới sự hỗ trợ của sóng siêu âm. Nhiều phương pháp đo lường tiên tiến khác nhau như nhiễu xạ tia X, kính hiển vi điện tử quét và quang phổ Raman, đã được sử dụng để kiểm tra các tính chất cấu trúc, hình thái, quang học của các hạt nano TiO ₂ . Kết quả chỉ ra rằng các hạt nano TiO ₂ có hình thái đồng nhất, giống hình cầu, hơn nữa kích thước hạt giảm đáng kể khi có sự hỗ trợ của sóng siêu âm. Phổ nhiễu xạ tia X và Raman đã cung cấp thêm các thông tin về các đặc trưng tinh thể cũng như các pha dao động mạng tinh thể của các hạt nano TiO ₂ , qua đó đã xác nhận sự hiện diện của pha anatase với độ tinh khiết cao. Phổ Raman đặc biệt làm nổi bật các chế độ rung động phonon tương ứng với các chế độ E _g , B _{1g} và A _{1g} , đặc trưng của pha anatase, chứng minh độ tinh thể được cải thiện khi xuất hiện sự hỗ trợ của sóng siêu âm. Hơn nữa, khi các hạt nano anatase TiO ₂ này được đưa vào dầu bôi trơn đã làm tăng hiệu suất cắt thép không gỉ AISI. Kết quả này thể hiện tiềm năng của phương pháp tổng hợp hạt nano TiO ₂ dưới sự hỗ trợ của sóng siêu âm trong việc phát triển các vật liệu hỗ trợ bôi trơn tiên tiến, hiệu suất cao.
Ngày hoàn thiện: 26/11/2024	
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TỪ KHÓA	
Hạt nano TiO ₂	
Pha Anatase	
Phương pháp điện hoá	
Hỗ trợ của sóng siêu âm	
Dầu bôi trơn	

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1. Introduction

In recent decades, nanomaterials, especially metal nanoparticles, have garnered significant attention due to their various technological applications, as highlighted in numerous studies. The unique properties of nanoparticles, which differ markedly from their bulk counterparts, have made them a subject of great interest among scientists [1], [2]. Among them, Titanium dioxide (TiO_2) nanoparticles, particularly those less than 100 nm in diameter, have emerged as a new generation of advanced materials with many applications. TiO_2 is one of the most extensively studied materials, especially in applications like solar cells, pollutant degradation, water photolysis, gas sensors, and various engineering-process applications owing to its excellent photocatalytic activity, non-toxicity, low cost and high stability [1], [3], [4].

The synthesis and stabilization of TiO_2 nanoparticles (NPs) are commonly achieved through the sol-gel, hydrothermal/solvothermal, chemical vapour deposition (CVD) and/or electrochemical method. The sol-gel method, widely used for synthesizing TiO_2 nanoparticles, involves the hydrolysis and condensation of titanium alkoxides to form a colloidal sol, which upon drying and calcination, yields TiO_2 nanoparticles [5], [6]. This technique is preferred for producing high-purity nanoparticles with controlled size and morphology. Yang H.M. and his group reported on the TiO_2 NPs prepared by sol-gel method which following an annealing process from 500 to 650 °C to promote the mono-phase anatase and mix-phase of anatase and rutile for reducing of methylene orange dye [6]. However, challenges like weak anatase crystallinity and poor mono-dispersity can impact their performance in specific applications. Hydrothermal/solvothermal methods construct TiO_2 nanoparticles under high temperature and pressure, with water and organic solvents. Furthermore, the dopants into TiO_2 structure were explored by the hydrothermal process which enhanced the efficient TiO_2 -based photocatalyst [7]. In addition, for the accurate control over nanoparticle size, shape, and crystallinity flexible on the thin film TiO_2 applications, the CVD is an adaptable technique. This method facilitates the deposition of TiO_2 NPs on various substrates, resulting in particularly valuable for applications requiring thin films or coatings, such as photovoltaic devices. Nevertheless, the process can be costly, involves high temperatures, and may produce hazardous by-products, limiting them for large-scale production [8]. These methods offer accurate control over nanoparticle size, shape, and crystallinity, making them suitable for high surface area. However, they require specialized equipment, extended reaction times, and pose challenges in scalability.

The electrochemical method is a highly effective approach for synthesizing TiO_2 nanoparticles. By employing controlled current electrolysis, it enables the deposition of highly crystalline anatase TiO_2 nanoparticles with precise control over size distribution, which can be finely tuned by adjusting current density and electrolyte composition. This method is particularly advantageous for producing nanoparticles with high purity and uniformity, essential for applications [9]. Moreover, the electrochemical method is straightforward and cost-effective, making it well-suited for large-scale production. Unlike other techniques that may require complex equipment or harsh chemical conditions, this method operates under relatively mild conditions, reducing the risk of contamination and material degradation. However, the primary challenges are the requirement for precise control of the electrochemical parameters, such as current density and electrolyte composition, to achieve consistent results. Variations in these parameters can lead to non-uniform particle size, crystallinity, and purity, which may affect the performance of the nanoparticles in specific applications. Another drawback is the potential for electrode degradation during the process, particularly if reactive electrolytes or high current densities are used. This can result in contamination of the nanoparticles and reduced efficiency of the synthesis process [10], [11]. Additionally, the method typically produces a relatively low yield of nanoparticles per batch, which might limit its efficiency in large-scale production unless optimized for higher throughput. To address these issues, the study proposes the synthesis of pure

anatase TiO₂ nanoparticles using an electrochemical method, specifically controlled the effectiveness of the reaction is crucial.

Herein, we report a simple route preparation of anatase TiO₂ NPs by using an electrochemical process with the assistance of the ultrasound wave. The synergistic of ultrasound energy with the electrochemical process would enhance both the cavitation phenomenon and the mass transport of oxidation–reduction reaction. Moreover, the ultrasound-assisted TiO₂ NPs synthesis plays a key role of developing advanced, high-performance lubricating systems.

2. Materials and experiment

2.1. Materials

Ti foils (99%), absolute Ethanol were purchased from China, NH₄NO₃ was purchased from Sigma Aldrich. The Simply soybean cooking oil was purchased from supermarket in Vietnam.

2.2. Prepare TiO₂ NPs

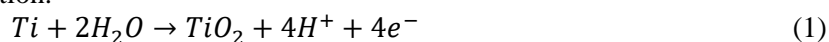
First, 200 mL of a 1 M NH₄NO₃ solution was prepared in a 250 mL beaker. The solution was stirred on a hotplate at 300 revolutions per minute (rpm) for 20 minutes at room temperature to serve as the electrochemical electrolyte. After stirring, the beaker was placed in a bath sonicator operating at 20 kHz and 80 W. Next, two titanium (Ti) foils, with the size of 1 cm in width, 5 cm in length, and 0.1 cm in thickness, were positioned 1 cm apart and immersed to a depth of 3 cm in the electrolyte. The foils were connected to the anode and cathode of a direct current power supply, with a constant voltage of 30 V applied for 30 minutes. Following the electrochemical process, the resulting TiO₂ nanoparticle suspension in the electrolyte was sonicated for 20 minutes. The powder product was then collected by filtration using a PVDF membrane with a 0.2 μm pore size. The collected powder was washed by ethanol and de-ionized (DI) water at least 3 times and then dried at 70 °C in the air for 3 hours and stored in a vial for further characterization. The sample prepared with ultrasound assistance is referred to as ultrasound-assisted TiO₂ nanoparticles (UA-TiO₂). A control experiment, conducted under similar conditions but without the use of ultrasound, produced a sample named non-ultrasound-assisted TiO₂ nanoparticles (NUA-TiO₂).

2.3. Characterization

Field emission scanning electron microscopy (FE-SEM) images were captured using a JEOL 6700 microscope, operated at an accelerating voltage of 15 kV. Raman spectra were obtained with a HORIBA LabRAM HR spectrometer, utilizing an Ar laser source with a 514.5 nm excitation wavelength. X-ray diffraction (XRD) analysis was carried out using a Bruker D2 diffractometer, equipped with a Cu Kα radiation source.

3. Results and Discussions

Figure 1 shows the experiment setup where 2 TiO₂ foils were connected to external anode and cathode of a DC supply power in sonicator bath. The electrochemical anodization is performed in 1 M NH₄NO₃ aqueous electrolyte. When the DC current goes through two electrode the Ti metal instantly starts to be transformed into TiO₂ NPs from the surface of anode connection foils. In the meantime, there is a vigorous bubble flow at the cathode connection foil. Under the synergistic of ultrasound energy, the formed TiO₂ on the anode foil peeled off and dispersed into the electrolyte. The next layer of Ti metal continues anodized by the same mechanism which following the reaction equation:



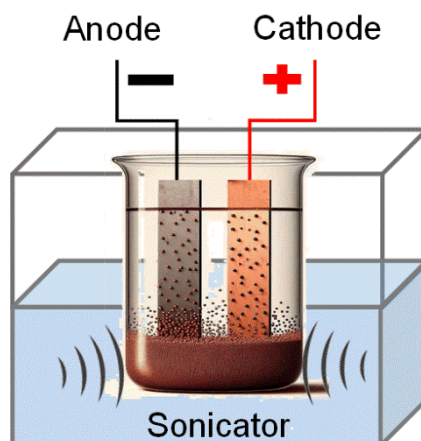


Figure 1. *Experiment setup*

Mass measurements using an analytical scale, taken before and after the TiO_2 synthesis experiment, indicated that a small amount of TiO_2 was produced from the Ti cathode foil. In contrast, the experiment without ultrasound support was performed under the same conditions for comparison. The electrochemical forming of the insulating layer TiO_2 during the process inhibits ionic diffusion from the electrolyte to the titanium anode, thereby slowing down the anodization process. Without the ultrasound activation, the electrochemical reaction was reduced and stopped after 8-10 min cause of the nonconductivity anode with the TiO_2 layer covering. In the case of the ultrasound application, the insulating layer of TiO_2 was dispersed in the electrolyte, resulting in the electrochemical reaction at the anode for forming TiO_2 NPs [12]. Therefore, the use of ultrasound is crucial for sustaining the electrochemical preparation of TiO_2 .

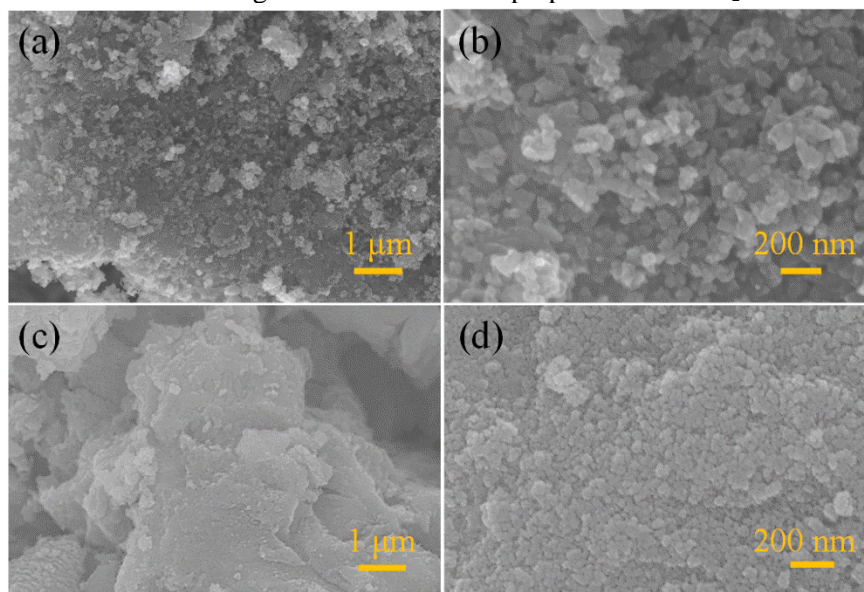


Figure 2. *SEM images with different magnification of (a), (b) NUA- TiO_2 NPs and (c), (d) UA- TiO_2 NPs*

The field emission scanning electron microscope (FESEM) was selected to compare the morphology different of TiO_2 NPs prepared by electrochemical anodization process. Figure 2 displays the SEM images of NUA- TiO_2 (a, b) and UA- TiO_2 (c, d) NPs at different magnification, respectively. The powder of TiO_2 NPs was stick on the carbon tape and annealing at 70°C for 3hr in the air. The prepared-sample were employed SEM at high voltage of 15 kV with the working

distant of 8 mm by using the JEOL 6700 FE SEM. The NUA-TiO₂ nanoparticles display a relatively uniform morphology, as depicted in Figure 2(a). However, upon increasing the magnification to 50K, significant differences in particle structure become evident, as shown in Figure 2(b). In contrast, SEM images of UA-TiO₂ nanoparticles, presented in Figure 2(c, d), reveal a highly uniform particle morphology with a notable reduction in particle size. While the NUA-TiO₂ sample exhibits a range of particle sizes between 50 nm and ~100 nm with varied morphologies, the UA-TiO₂ sample consists exclusively of spherical particles with sizes ranging from 10 to 20 nm. These results suggest that ultrasound assistance not only sustains the electrochemical reaction but also significantly influences both the reduction in particle size and the enhancement of morphological uniformity in TiO₂ nanoparticles.

To comprehensively investigate the effect of ultrasound on the structural properties of TiO₂ NPs, X-ray diffraction (XRD) and Raman spectroscopy were employed. Figure 3(a) illustrates the XRD patterns of the NUA-TiO₂ and UA-TiO₂ samples, represented by the dark and red curves, respectively. XRD analyses were conducted over a 2θ range of 20° to 80° to assess the crystalline structure of the samples in detail. The diffraction peaks observed at 2θ values of 25.3°, 38.0°, 47.7°, 54.3°, and 62.6° are associated with the (101), (004), (200), (105), and (204) crystal planes, respectively, corresponding to the anatase phase of TiO₂, this results highly agreed with previously reported [13], [14]. In addition, the UA-TiO₂ sample exhibits significantly sharper and more intense diffraction peaks compared to the NUA-TiO₂ sample, indicating a higher crystallinity in the ultrasound-assisted synthesis. The lower intensity and broader diffraction peaks observed in the NUA-TiO₂ sample suggest the presence of an amorphous phase and a mixture of anatase and rutile phases in the TiO₂ structure [7].

Figure 3(b) presents the Raman spectra for both UA-TiO₂ and NUA-TiO₂ samples, obtained using a 532 nm He-Cd laser source directed onto the powder samples placed on a glass substrate. In the Raman spectrum of the NUA-TiO₂ sample, only a single, prominent peak is observed at a wavenumber of 147.9 cm⁻¹, corresponding to the E_g mode, which is characteristic of the anatase phase of TiO₂. In contrast, the Raman spectrum of the UA-TiO₂ sample reveals four feature peaks, corresponding to the E_g, B_{1g}, and A_{1g} modes, which are typically associated with the anatase phase. The appearance of these additional peaks in the UA-TiO₂ sample suggests a higher crystallinity, as well as potential size effects influencing the Raman response [15]. This contrast in peak sharpness and intensity underscores the role of ultrasound in enhancing the crystallinity of TiO₂ nanoparticles during synthesis.

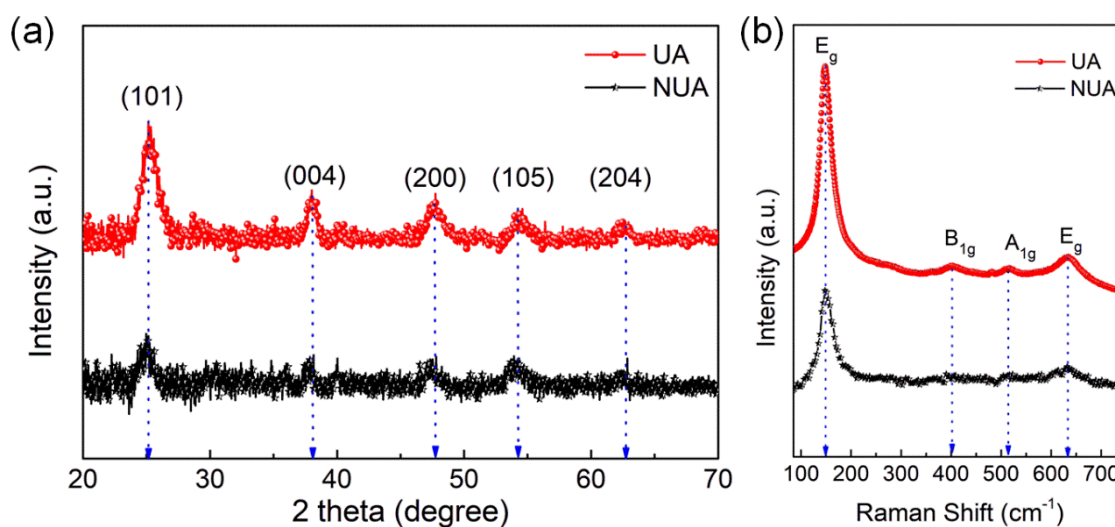


Figure 3. (a) XRD patterns and (b) Raman spectra of NUA-TiO₂ and UA-TiO₂

To examine the application of anatase phase TiO_2 NPs on the affection of the mechanical processing, the additives including nanoparticles were used as the lubricant of the cutting of AISI 304 stainless steel rod. TiO_2 NPs, both NUA- TiO_2) and UA- TiO_2 were dispersed at a concentration of 1 wt% in Simply soybean cooking oil and sonicated for 20 minutes before being applied during the cutting process. The cutting was conducted using a mini cutter machine equipped with a circular saw blade, and the lubricant was sprayed onto the cutting region both before and during the operation. Analysis of the cutting surface, performed using a digital microscope, revealed that without lubricant, the surface displayed a rough texture and a blue discoloration as shown in Figure 4(a). In contrast, the application of the nanofluid lubricant resulted in a smoother, white surface, indicating a significant enhancement in cutting performance as revealed in Figure 4(b,c). This improvement is attributed to the reduction in friction and temperature facilitated by the TiO_2 NPs, which reduces the cutting force required. TiO_2 nanoparticles exhibit excellent hardness, heat resistance, and wear resistance. When added to cooking oil, they enhance its anti-wear properties. Due to their strong adsorption capacity, TiO_2 nanoparticles absorb more cutting fluid, increasing fluid presence at the tool/workpiece interface. With unsaturated bonds, their surface atoms readily bind to polar atoms in cooking oil, raising surface energy and improving lubrication [16]. Notably, no apparent difference was observed between the effects of UA- TiO_2 and NUA- TiO_2 , possibly due to the limited resolution of the digital microscope used in the study. These results highlight the potential of TiO_2 nanofluids in improving the efficiency and quality of the cutting process in stainless steel.

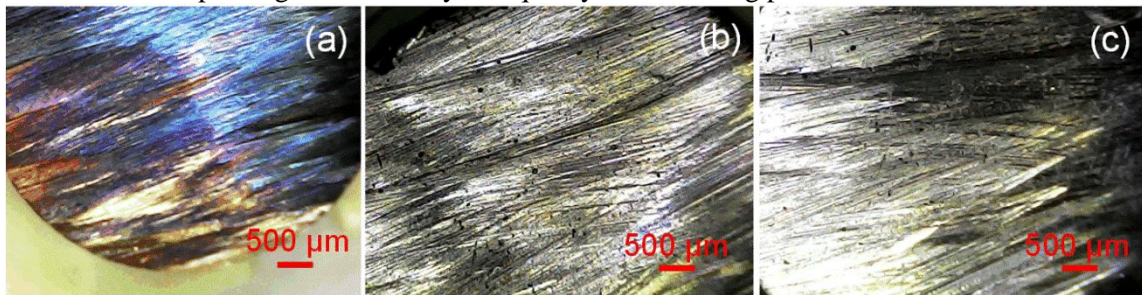


Figure 4. Cutting surface of AISI 304 stainless steels (a) without lubricant (b) NUA- TiO_2 NPs blends oil and (c) UA- TiO_2 NPs blends oil additive

4. Conclusion

In this research, anatase phase TiO_2 nanoparticles (NPs) were synthesized through an electrochemical method supported by ultrasound assistance. SEM images confirmed the production of high-quality, uniformly spherical nanoparticles, with sizes ranging from 10 to 20 nm. XRD patterns and Raman spectroscopy analyses revealed that the ultrasound-assisted synthesis resulted in nanoparticles with enhanced crystallinity. The synthesized anatase TiO_2 NPs were found to be effective lubricants in cutting processes. This obtained study suggest that TiO_2 NPs could be a valuable lubricant in practical applications, offering improved performance in machining operations.

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