Title : Protons ions beam irradiation of TiO2 nanoparticles

Abstract:

This research aims to explore the potential effects of proton ion beam irradiation on TiO2 nanoparticles. Based on the capabilities of an accelerating proton beam, nanoparticle properties could potentially be modified to improve their performance for various applications. This work aims to further understand the possible unique modifications that can be introduced into TiO2 nanoparticles under proton irradiation. Our work investigates the revolutionary potential of proton ion beam irradiation on nanoparticles TiO2. Proton irradiation creates pathways to manipulate traditional nanoparticle properties, offering controlled opportunities to influence their performance for various applications. We address the complex modifications proton irradiation causes to TiO2 nanoparticle properties, paving the way for the realization of nanoparticle properties . By exploring the modifications and conducting extremely detailed analysis to gain a better understanding of the materials. The analysis would lead to an increased basic understanding of the modifications and uncover more about nanoparticle functionalities following proton ion beam irradiation.

Introduction:

The properties of titanium dioxide nanoparticles have attracted much attention for various applications, including photocatalysis, sensing, and storage. Although titanium dioxide nanoparticles have been studied and developed for many years, their properties can still be enhanced, tuned, and improved. Proton ion beam irradiation was known as one of the ideal methods to control, modify the structure, and properties of materials at the nano- and micro-scale levels. Applied with proton irradiation, titanium dioxide nanoparticles can be modified with structural changes, optimizing for various applications. Therefore, the proton ion beam irradiation is a highly promising method to control, manipulate, tune up the properties of titanium dioxide nanoparticles on the nano-scale level. Different kinds of modification processes, from structural to chemical, are enabled, help to boost the performance of titanium dioxide nanoparticles in many applications. Proton irradiation can induce several modifications of titanium dioxide nanoparticles, including generated interstitials defects and dopants, phase change, and morphology, and surface chemistry adjustment . These all can create effects on some properties of titanium oxide nanoparticles, such as optical absorption, band structure, charge carrier dynamics, and surface chemistry and reactivity. Furthermore, proton irradiation enables the creation of various nanostructures and interfaces, which can help to improve the performance even further. Defect and dopant formation can enhance charge transfer process and recombination loss, improve the catalytic activity of nanoparticles. To sum up, surface functionalization can be used to improve the biocompatibility of any nanoparticles, while the stability of sensing can rise due to the modification of ion bunk. In its turn, proton ion beam irradiation helps to control the dose, energy, and spatial distribution of irradiation in much greater detail and thus modify nanoparticles specifically for a certain application. Together with these factors and their systematic variations, it is possible to find the optimal TiO 2 nanoparticle properties for all mentioned abovementioned applications, such as environmental treatment and water purification, solar energy conversion and systems, and biosensing devices. Hence, proton ion beam irradiation can be considered as a promising direction for further TiO 2 nanoparticle development and engineering. Due to systematic exploration and improvements, it might be used to solve many of the current problems in many fields, such as catalysis, sensing, energy transfer, and biomedical applications or to find new possible ways.

Literature review :

Proton beam irradiation of TiO 2 nanoparticles has been the focus of much interest in recent studies.

Gerken et al (2022) state that the study explores the potential of nanoparticle-based radioenhancement in improving the effectiveness of radiotherapy. Various metal oxide nanoparticles, along with TiN and Au nanoparticles, were investigated for their radioenhancement mechanisms under different irradiation conditions. While Au nanoparticles showed exceptional performance under certain settings, their efficacy diminished in clinically relevant conditions. Conversely, HfO2 nanoparticles retained some effectiveness, and TiO2 nanoparticles displayed significant efficacy across all conditions due to their unique properties. The findings offer insights for designing nanoparticle radioenhancers tailored to different radiotherapy modalities, paving the way for improved precision in treatment [1].

Lin et al.(2023) drew attention to the Gold nanoparticles have the potential of radiosensitizing photon and proton beam radiation therapy. This study developed a biological model to assess GNP impact towards cell survival post irradiation with megavoltage and proton photon and kilovoltage in the proton beam. Kilovoltage photons indicated the most enhancement as they showed substantial interaction with the GNPs. The results indicated that GNPs significantly hindered cell survival in proton and MV photon beam irradiation, with the nucleus internalization being more effective. Therefore, smaller GNPs do enhance sensitization. Additionally, no expansion was discovered continuing proton therapy when GNPs were not internalized into the cytoplasm. If the internalization has happened mainly in the cell nucleus, GNP may be suitable for proton radiotherapy [2].

Kim et al.(2012) have since established that Protons interacting with metallic nanoparticles cause a substantial release of MNP-induced secondary electrons and characteristic x-rays . Investigating if MNP secondary radiations have the potential to improve protons therapeutic effect, researchers irradiated tumors of four million C57BL/6 CT26 tumor cells grafted with 100 to 300 mg/kg MNP intravenously for 2.5 hours before applying a single dose of proton radiation to four groups of mice to between 10 to 41 Gy. An irradiation of a defined Bragg peak of the nanoparticle with a proton beam was carried out such that the Bragg peak only fully absorbed within the tumor volume and another after traversing the whole body. The study showed an increased CTR with the absorbed dose from 37% – 62% and the traversing irradiation group from 50% – 100% respectively, compared to the proton irradiation alone group, $p < 0.01$. In contrast, the one-year survival rate increased from 58% – 100%, while proton irradiation group had a survival rate of 11% -13%. Intracellular ROS levels increased from 12% – 36% at 10 Gy for cells treated with protons compared to protons only treated cells [3].

Tripathy et al.(2015) investigated the impact of swift heavy ion irradiation on diverse properties of TiO_2 such as structure, optics, and microstructure. The TiO_2 nanoparticle pellets were irradiated with 120 MeV Ag ions for fluences differed from 5 × 1011 to 1 × 1013 ions cm−2. A combination of analytical methods such as X-ray diffraction (XRD), Raman spectroscopy, UV–visible spectroscopy, and photoluminescence studies showed that the original and irradiated pellets preserved the anatase phase. The XRD analysis indicated a particle crystallite size of around 16 nm close to the upper limit compatible with the anatase phase's stability. This emphasizes that the initial microstructure plays a key role in the nanoparticles' response to irradiation. Even though a crystal structure is preserved and anatase TiO_2 is polycrystalline, the crystalline volume fraction significantly decreased after exposure to irradiation. Poisson fitting, which connects the irradiation fluence with the suppression of the XRD peak area, determined a track radius of about 2.1 nm through each 120 MeV Ag ion across the TiO_2 nanoparticles [4].

Jones et al (2021) observed that the radiobiological effectiveness of TiO_2 nanoparticles can be dependent on the energy level of the protons used to irradiate the nanoparticles. This requirement may be attributed to the need for optimal parameters for proton beam use to enhance its therapeutic impacts [5].

Farooq at el (2021) state that one of the most promising avenues for simultaneously increasing the efficiency of radiotherapy and reducing its damaging potential is radioenhancement via nanoparticles. The outcomes of preclinical and clinical research in this field have already been promising; although the underlying processes, such as the dependence of effectiveness on nanomaterial composition and irradiation technology, remain poorly understood. This paper examines the mechanisms of radioenhancement for several selected metal oxide nanoparticles : SiO_2 , TiO_2 , WO_3 , HfO_2 , TiN, and Au nanoparticles, under several radiotherapy types with photons with 150 kV p and 6 MV, and protons with 100 MeV beamline [6].

Ahmad at el (2020) demonstrates that each of the investigated nanoparticles has a dramatically different profile of performance. While the Au nanoparticles are highly efficient when the kV irradiation dominates due to photoelectric effect, the more relevant clinical MV photon and proton irradiations reduce their efficacy significantly. Conversely, HfO_2 nanoparticles retain their efficiency under MV photon and proton therapies. A surprising finding was the radioenhancing effects of TiO_2 nanoparticles, even despite a lower Z_{eff} due to its radiocatalytic radiochemistry, resulting in the formation of hydroxyl radicals, as well as its nuclear interactions with protons. A comprehensive dataset on radioenhancement in different ionizing radiation fields is obtained, allowing for the development of frameworks on the creation of radiation therapy-specific radioenhancers and nanomedicines based on them. This study lays the foundation for fully understanding the possible nanoparticle processes in radioenhancement and the development of ideal nanotheranostics [7].

Haq AT EL (2021) state that the TRAX Monte Carlo code was used to investigate potential dose enhancement effects around nanoparticles composed of various atomic number high atomic number materials when irradiated with protons or electrons . Fe, Ag, Gd, Pt, and Au nanoparticles with 22 and 2 nm radii were irradiated with monoenergetic proton beams of 2, 20, and 300 MeV and 44 keV electrons. As opposed to primary ionization, Auger cascades released many electrons due to the high number of electrons in atoms with high atomic numbers . The effect of Auger electrons from the nanoparticles on additional nanoscopic radial dose contributions was analyzed by comparing it to liquid water and water simulated to the atomic vicinity of the metallic materials. Comprehensive sets of low energy electron cross sections for the nanoparticle materials were specifically evaluated [8].

Smith at el (2019) established an investigation on a newly developed proton exchange membrane fabricated with sulfonated polyethersulfone and modified TiO2 nanoparticles for fuel cell application. A new approach to modify an existing TiO2 nanoparticle through sulfonation and polyaniline coating was introduced. Comprehensive analysis was performed, including water uptake , swelling ratio , methanol uptake , ion exchange capacity , chemical stability, and thermal property measurement. The new polymer matrix's surface and structural features were analyzed by Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared (FTIR), and X-ray Diffraction . A composite membrane with 0.5% PANI-modified TiO2 showed the highest proton conductivity at 2.30×10^{-4} S/cm, which proposed the combined effect of the PANI amine group and sulfonic acid group in modified TiO2. Moreover, the composite membrane showed excellent thermal and chemical stability, which reveals the potential of using the composite membrane in fuel cell application [9].

Problem Statement:

While TiO2 nanoparticles have been thoroughly researched, there is an ongoing need to investigate new methods that could further improve their properties. Although traditional synthesis paths have made it possible to obtain these materials with some preferred characteristics, their outcomes appear to be difficult to predict. As a result, the whole class of synthesis techniques should be researched and changed if necessary. The ion beam treatment used in the form of proton ion beam irradiation offers the possibility to modify the properties of TiO2 nanoparticles with splendid accuracy. However, it is quite a novel feature that has not been fully discovered to date.

Proton ion beam irradiation constitutes a feasible avenue for addressing this issue. While conventional routes for synthesis mainly integrate chemical and physical processes to shape the properties of nanoparticles, proton irradiation provides a unique opportunity for the precise manipulation of their structure and characteristics at the atomic level. Thus, the selective exposure of TiO2 nanoparticles to proton beams is associated with controlled modifications that include aged engineering, the incorporation of distinct elements, and surface functionalization. As a result, these outcomes allow the material to be personalized in terms of its properties to meet the requirements of different functional applications. Nevertheless, the application of proton ion beam irradiation for the alteration of TiO2 nanoparticles implies a comprehensive understanding of its effects on the material. Due to the intricacies of the nanoparticle systems and the correlations between irradiation parameters and achievable properties, a comprehensive study of the corresponding effects is required to develop-in-depth knowledge of the processes and optimize the indicated procedure for the anticipated outcomes. Therefore, the need for such a thorough investigation on the effects of proton irradiation on TiO2 nanoparticles valid results the focus on directed research that helps to make an informed decision and supports the development of differentiated nanoparticle materials with the improved background activity.

Research Objectives:

The main goals of the current work are to analyze the impacts of proton ion beam irradiation on TiO2 nanoparticles. The main objectives include the following:

- To study structural and morphological features affected by proton irradiation in TiO2 nanoparticles.
- To analyze the irradiation effect on the optical and electronic properties of TiO2.
- To make an evaluation of proton-implanted TiO2 nanoparticles in terms of their applications in photocatalysis, sensing, etc.

Methodology:

Synthesis of TiO2 Nanoparticles:

1. **Material Preparation:**
    - Pure titanium foil (0.127 mm thickness, 99.8% purity, Alfa Aesar) will be utilize
    - Electropolishing will be perform for the titanium foil.
    - Three-step sonication will be conduct to attain acetone, isopropyl alcohol, and deionized water.

2. **Electrochemical Anodization:**
    - Two-electrode cells with Pt mesh will be used as the counter electrode.
    - The back of the Ti foil will packed with tape for uniform current distribution and protection.
    - The titanium foil will be anotize for 10 minutes under a constant voltage of 15 V.
    - Electrolyte solution consisting of 0.36 M ammonium fluoride in 95 vol% formamide and 5 vol% deionized water will be utilize.
    - Ultrasonic cleaning of anodized samples will be perform in deionized water for 30 seconds.
    - TiO2 nanotubes will be added in a mixture of ultra-pure 20% O2/balance Ar gas at 450 °C for 4 hours to obtain anatase TiO2.

Proton Beam Irradiation:

3. **Experimental Setup:**
    - Mount TiO2 nanoparticle films onto a copper irradiation stage will equipped with embedded heating elements and thermocouples.

- Measurement of ion fluence will be accurate by using a standard four-corner Faraday cup assembly.
- Pressure will be of 4 × 10−7 torr throughout the irradiation process.

4. **Proton Beam Irradiation:**
   - 200 kV Danfysik ion implanter will be utilize to irradiate TiO2 nanoparticle films with 195 keV protons.
   - Implement a raster-scanning technique to achieve uniform irradiation across the samples ,a raster-scanner technique will be use.
   - Sample temperature during irradiation will be moniter by using embedded thermocouples.
   - Irradiation damage profile will be calculate by using the Stopping and Range of Ions in Matter (SRIM-2013) program, considering the limitations in depicting nanotube structures.

Characterization and Analysis:

5. **Electrochemical Testing:**
   - Li half-cells wiil be assemble in coin-type cells with appropriate electrodes and electrolyte.
   - Perform galvanostatic cycling will be perform with current in between 2.5 and 0.9 V versus Li/Li+.
   - Electrochemical impedance spectroscopy (EIS) and Mott–Schottky measurements will be concuct by using three-electrode cells.
6. **Characterization Techniques:**
   - Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) will utilize for having structural characterization.
   - Employ Raman spectroscopy and X-ray diffraction (XRD) will be use for analyzing the structural properties of TiO2 nanoparticles.
   - out-of-plane conductivity of nanotubes will be determine through electrical conductivity measurements.

Expected outcome

This study on proton beam irradiation of TiO2 nanoparticles is expected to yield significant findings across multiple fronts. It will provide a detailed characterization of the irradiation damage profile, highlighting structural alterations induced by proton irradiation. This will be complemented by a demonstration of enhanced electrochemical properties, showcasing the potential for improved performance in lithium-ion battery applications. Additionally, the study will elucidate structural and morphological changes, detect crystallographic phase transformations, quantify alterations in electrical conductivity, and contribute to a broader understanding of radiation damage effects. These outcomes collectively will not only advance our knowledge of nanomaterial behavior under irradiation conditions but also pave the way for the development of tailored materials with enhanced properties for various technological applications.

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