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Self-assembly and morphological analysis of Fe^{3+}-doped TiO_2: from nanoparticles to nanofibers

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ABSTRACT

The morphology of nanostructured materials has an important role in determining their activity and functional properties, both in photocatalysis, sensors, optoelectronic devices, nanomedicine, energy storage and renewable energy applications. Various studies have shown that unique morphologies, such as nanofibers, can significantly improve the performance of materials in a variety of applications. In this context, titanium dioxide (TiO_2) doped with transition metal ions, such as Fe^{3+}, has attracted attention due to its potential for improved optical and magnetic properties. This study aims to understand how the self-assembly process can produce nanofiber morphology in Fe^{3+}-doped TiO_2, as well as analyze the effect of doping on changes in morphology and material properties. Through the process of hydrothermal synthesis, Fe^{3+}-doped TiO_2 is developed from a nanoparticle structure into a nanofiber. The morphology and properties of the material were analyzed using Scanning Electron Microscopy (SEM). The results showed that Fe^{3+} doping affected the self-assembly process which led to the transformation of nanoparticles into nanofibers.

1. Introduction

The development of material technology, particularly nanotechnology, has revolutionized numerous fields, including renewable energy and medicine. Nanomaterials possess unique properties due to their tiny particle size, which differentiates them from conventional materials [1]. Titanium dioxide (TiO_2) is one of the most studied nanomaterials because of its wide applications in photocatalysis, gas sensors, optoelectronics, energy storage, and nanomedicine.

However, TiO_2 has limitations, particularly its large band gap of 3.2 eV, which restricts its ability to absorb visible light, limiting its efficiency in applications like sunlight-driven photocatalysis. To overcome this, researchers have explored doping TiO_2 with transition metal ions like Fe^{3+} to reduce the band gap and extend the material's light absorption range.

Doping not only affects the optical and electronic properties of TiO_2 but also impacts its morphology an important factor in determining the material's performance. The shape and size of nanoparticles significantly influence properties such as light interaction, electron transport, and chemical stability [2]. Nanofibers, for example, offer better electron transport and larger surface areas than nanoparticles, making them advantageous in applications

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like sensors and energy storage. Research has shown that TiO_2 nanofibers improve photocatalytic activity and energy storage capacity compared to their nanoparticle counterparts [3, 4].

One fascinating area of research is the morphological transformation from nanoparticles to nanofibers. This process can be driven by self-assembly, were nanomaterial structures form spontaneously due to particle interactions. In Fe^{3+}-doped TiO_2, doping influences both the electronic properties and particle interactions, facilitating the formation of nanofibers. These nanofibers exhibit enhanced surface area and electron transport, contributing to improved performance in applications such as photocatalysis and gas sensors. Additionally, Fe^{3+} doping introduces magnetic properties to TiO_2, opening the door to new applications in magnetic separation and data storage.

Previous research has shown that nanofiber structure can provide significant advantages in terms of electron transport and surface interactions, but not many have attributed these changes to Fe^{3+} doping in the context of nanofiber formation. Shymanovska et al, 2022 revealed the potential of Fe doped TiO_2 with various concentration ions for applications in photocatalysis, but specific research on the self-assembly mechanism and the effect of Fe^{3+} concentration on the morphology of TiO_2 nanofibers is still necessary [5]. Therefore, this study not only adds to the knowledge of the effect of Fe^{3+} doping on the morphology of TiO_2, but also provides new insights into the potential applications of nanofibers in various fields, including photocatalysis, energy storage, gas sensors and biodegradable and antibacterial polymer [6-9].

Nanofibers also have significant potential in nanomedicine, particularly in drug delivery, where their morphology allows for better targeting and interaction with cells. Studies have demonstrated that TiO_2 nanofibers improve drug absorption and retention in target cells compared to nanoparticles [10].

This study focuses on synthesizing Fe^{3+}-doped TiO_2 nanofibers using the hydrothermal method, which enables controlled morphology and uniform doping. By varying synthesis conditions such as doping concentration, the research aims to understand how these factors influence the formation of nanofibers and their functional properties, including optical and magnetic characteristics.

The findings from this research are expected to advance the development of efficient and multifunctional nanostructured materials, with potential applications in photocatalysis, energy storage, sensors, and nanomedicine. Understanding the relationship between morphology, doping, and material properties will contribute to the future of nanotechnology in various industries.

2. Methodology

2.1. Materials and Instrumentals

The materials used for synthesis Fe^{3+}-doped TiO_2 consisted of pure Titanium dioxide (TiO_2) (P25 Degussa) 99.9%, iron(III) chloride 97%, sodium hydroxide pellets (NaOH) 98%, and deionized water. The instrument used for morphological analysis is performed with Scanning Electron Microscopy (SEM).

2.2. Methods

2.2.1. Synthesis of Sodium Titanate Nanofibers

Sodium titanate nanofibers were prepared using a hydrothermal method as previously reported [11]. Briefly, 0.125 g of TiO2 nanoparticles were mixed with 10 M alkali solution and placed on a magnetic stirrer for 2 hours, the Fe^{3+} doped TiO_2 Nanofiber prepared by mixing the iron salt into the sodium TiO_2, followed by ultrasonic sonication for 15 minutes to form a milky white suspension. The suspension was then transferred to a Teflon-lined autoclave and heated at 180°C for 24 hours. The sample was collected after cooling to room temperature and subsequently washed repeatedly with distilled water until neutral pH was achieved to obtain sodium titanate nanofibers.

Once the hydrothermal process is complete, the resulting product is filtered and washed several times using deionized water and ethanol to remove the remnants of the reagent. The final product is then dried at 80°C and calcined at 500°C for 2 hours to increase crystallinity.

3. Result and Discussion

3.1. Morphological Evolution from Nanoparticles to Nanofibers using Scanning Electron Microscopy (SEM)

Morphological observations of TiO_2 materials using Scanning Electron Microscopy (SEM) provide valuable insights into the structural evolution from nanoparticles to nanofibers. Figure 1 demonstrates that the commercial TiO_2 P25 structure, initially composed of nanoparticles approximately 50-100 nm in diameter, transforms after hydrothermal synthesis in an alkaline NaOH solution. This process triggers self-assembly, resulting in a microwire structure several micrometers long. The introduction of Fe^{3+} ions further alters the morphology [12], producing microfibers with a shape resembling palm tree leaves, and the concentration of Fe^{3+} doping significantly influences this transformation.

The self-assembly process is driven by the oriented attachment mechanism**,** wherein nanoparticles merge through specific crystal interactions to form longer, more directional structures [13]. Under hydrothermal conditions, high temperatures and pressures accelerate atom diffusion, facilitating the formation of regular crystal structures. In an alkaline environment, these nanoparticles aggregate and align along specific crystal directions, leading to the development of one-dimensional structures like nanofibers.

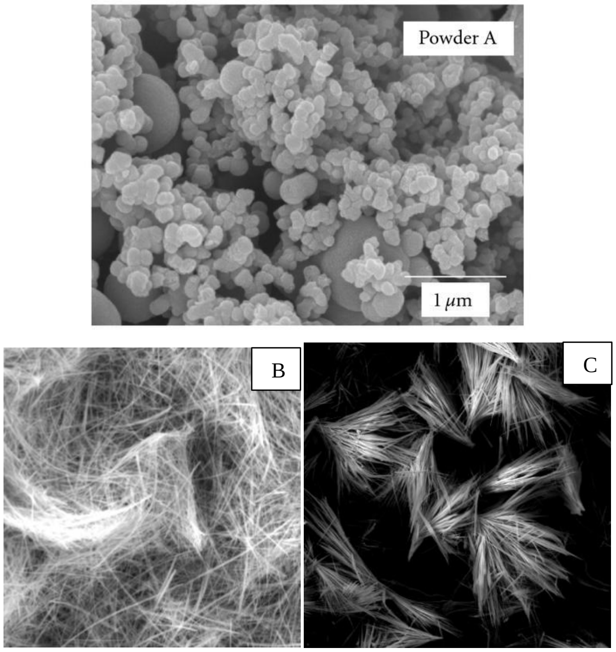

Fig. 1. Morphological Evolution from Nanoparticles to Nanofibers using Scanning Electron Microscopy (SEM): a) nanoparticles; b) TiO_2 nanofiber; and c) Fe^{3+} doped TiO_2 Nanofiber

The formation mechanism of Fe^{3+}-doped TiO_2 nanofibers starts from small nanoparticles in an alkaline solution. The addition of Fe^{3+} ions changes the electronic properties and improves the interaction between the particles, facilitating self-assembly under hydrothermal conditions. This process results in anisotropic growth, in which the fibers are formed longer with a consistent diameter. High pH conditions and increased temperatures accelerate the diffusion of atoms, reducing the recombination of hole-electron pairs. The Fe^{3+} ions play a crucial role in this self-assembly process, as they modify surface tension, promoting nanofiber growth. Fe^{3+} doping not only impacts surface tension but also promotes anisotropic growth, encouraging the formation of nanofiber structures. By altering surface energy and interparticle interactions, Fe^{3+} ions increase the likelihood of nanoparticles merging in specific directions. Additionally, hydroxide ions (OH^-) from the alkaline solution help direct particle growth. At high pH, OH^- ions affect crystallization conditions, interacting with nanoparticles and influencing surface reactions, further promoting the formation of nanofibers [14].

The morphological transformation of Fe^{3+}-doped TiO_2 from nanoparticles to nanofibers demonstrates significant structural changes as synthesis conditions progress. The self-assembly process, driven by nanoparticle alignment and the effects of Fe^{3+} doping, is essential for the development of long nanofiber structures. After the hydrothermal process, the resulting product is filtered and washed several times to remove any residual reagents that can contaminate the material, as well as to achieve a neutral pH that is important for the stability and reactivity of the product. Hydrothermal conditions, alkaline environments, varying Fe^{3+} concentrations, and washing treatment all contribute to the growth mechanism and morphological outcome. A deeper understanding of these processes could lead to the creation of nanostructure materials with enhanced properties, applicable in fields such as technology and medicine.

3.2. The Role of Self-Assembly Processes in Improving Functionality

The self-assembly process is an important phenomenon that plays a major role in the formation of a more organized and uniform nanofiber structure in Fe^{3+}-doped TiO_2 research. Self-assembly can be defined as the process by which small particles (such as nanoparticles) spontaneously form larger structures through interactions between particles, without requiring significant external intervention [15]. The doping concentration of Fe^{3+} had a significant effect on the morphological transformation of TiO_2 from nanoparticles to nanofibers. At low concentrations, the nanoparticles remain intact, but increased doping promotes more directed growth of nanofibers with stronger interparticle interactions. Fe^{3+} ions lower surface energy and favor anisotropic growth, where the properties of the material vary based on the direction of their growth. SEM analysis shows a clear transition to nanofibers at high molar ratios, but concentrations that are too high lead to agglomeration and reduce functional efficiency. This transformation improves the material's ability to absorb light and transport electrons, making it more efficient for functional applications. In the context of this study, the process facilitates the transformation from nanoparticles to nanofibers through an oriented attachment mechanism, where nanoparticles combine in a directional manner and form an elongated one-dimensional structure.

The nanofiber structure resulting from the self-assembly process has significant functional advantages, especially in terms of electron transport and photocatalytic efficiency. In semiconductor materials such as TiO_2, one of the main challenges is the recombination of electron-hole pairs that occurs after the material absorbs photons. This recombination can reduce photocatalytic efficiency because the excited electrons return to their ground state before they can be used for chemical reactions [16]. Therefore, structures that can improve electron separation and transport are highly desirable.

3.2.1. Increased Electron Transport

One of the main benefits of forming nanofibers through self-assembly is the increased electron transport which is more efficient compared to nanoparticle structures. Elongated nanofibers provide a longer continuous path for electrons to move. In nanoparticle structures, electrons are often trapped or recombined because they have to jump boundaries between particles [17]. In contrast, in nanofibers, electrons can travel along the fiber without needing to cross many interface boundaries, which can reduce electron-hole recombination.

This more efficient electron transport is essential in photocatalysis and energy storage applications, such as in batteries and supercapacitors. In photocatalysis, electrons produced from excitation by light must reach the surface of the material to initiate a photocatalytic reaction. With nanofibers, electrons have a greater chance of reaching the surface without undergoing recombination, thereby increasing the efficiency of the photocatalytic process. This is particularly important in pollutant degradation or heavy metal reduction applications, where electrons and holes play a role in the breaking of strong chemical bonds on target molecules. In addition, nanofibers provide more surface area and longer separation paths due to their unique shape and structure. First, with a very small diameter and relatively large length, nanofibers have a high aspect ratio, which means that the volume of material can be arranged in an elongated shape. This significantly increases the surface area per unit volume, allowing for more interaction with the surrounding environment, such as reactant molecules or light.

3.2.2. Electron-Hole Recombination Reduction

The self-assembly process also helps to reduce the rate of recombination of electron-hole pairs. The organized structure of the nanofibers allows for more effective separation of electrons and holes. In less organized structures, such as nanoparticles, holes and electrons often interact again due to the close distance between the hole formation center and the electron. Nanofibers provide more surface area as well as longer separation paths, so electrons and holes can be separated further from each other, reducing the possibility of recombination.

In addition, doping with Fe^{3+} ions plays a role in lowering the recombination energy by introducing additional energy levels in the TiO_2 band gap. This energy level acts as a trap that can hold electrons and make it easier for them to move towards the surface before they meet the hole, reducing the likelihood of recombination. This effective separation is essential in a variety of technology applications, including sensors and solar cells. In TiO_2-based sensors, the material works by detecting changes in electric current due to the interaction between electrons in the material and the target gas or molecule. By reducing recombination, the sensor signal becomes stronger and more sensitive, allowing for the detection of lower concentrations of substances [18]. In solar cells, efficient separation of electrons and holes is essential to improve the efficiency of energy conversion, so that more photons can be converted into electricity [19].

3.2.3. Effect of Self-Assembly on Morphological Control

The self-assembly process also plays an important role in controlling the morphology of materials, which in turn affects their functional properties [20]. By understanding the self-assembly mechanism, it is possible to control the length, diameter, and neatness of the nanofibers formed. Factors such as temperature, pressure, and dope concentration (Fe^{3+}) can affect how nanoparticles combine and form an orderly nanofiber structure. At higher concentrations of Fe^{3+}, for example, the formation of nanofibers becomes more regular and uniform, which is directly correlated with improved functional performance in energy storage and sensor applications. In the context of morphology, the structure of TiO_2 nanofibers formed during self-assembly offers a longer, directional path for electron transport. This path helps improve the efficiency of hole-electron pair separation, as electrons can travel further before meeting the hole. When electrons manage to avoid recombination, they can contribute to the growth and formation of more nanofibers, as the process often involves precipitation or binding from the solution.

3.2.4. Applications in Energy Storage and Sensors

In energy storage applications, such as lithium-ion batteries or supercapacitors, the longer, organized structure of the nanofiber allows for more efficient storage and release of electrons. Materials that have better electron transport and a larger surface area tend to have higher energy storage capacities and longer cycle times. In gas sensor or chemical sensor applications, nanofibers provide a wide surface for interaction with target molecules, as well as better electron transport paths, thereby improving the sensitivity and response speed of the sensor [18].

Several key parameters affect the formation of TiO_2 nanofibers through self-assembly. The doping concentration of Fe^{3+} is important to facilitate interactions between nanoparticles; too high can inhibit formation. The pH level of the alkaline solution also has an effect, where a high pH increases the solubility of the nanoparticles. The temperature and time of the hydrothermal accelerate the diffusion of atoms, favoring the formation of directional structures. The ratio of TiO_2 to alkaline solution affects the distribution of nanoparticles, while the stirring method and pressure conditions in the autoclave are also important. Optimizing these parameters helps to produce TiO_2 nanofibers with better functional properties.

Thus, the self-assembly process in the formation of TiO_2 nanofibers is inspired by the importance of better electron transport and more effective separation of electron-hole pairs, resulting in improved performance in a variety of technology applications, including photocatalysis, energy storage, and sensors.

4. Conclusion

This article examines the morphology of Fe^{3+}-doped TiO_2 and its transformation from nanoparticles to nanofibers through a self-assembly process. This study showed that Fe^{3+} doping on TiO_2 not only changes the morphology of the material, but also introduces weak ferromagnetic properties as well as improves the absorption ability of visible light. The results showed that the self-assembly process produced a nanofiber structure from TiO_2 that reduced the band gap size from about 3.2 eV to 2.7–2.9 eV. With these morphological changes, Fe^{3+}-doped TiO_2 becomes more efficient in a variety of applications, including photocatalysis and magneto-optical devices. This research provides new insights into the mechanisms underlying the formation of nanofiber structures and their impact on the functional properties of materials, which could expand the applications of nanomaterials in the fields of renewable energy, sensors, and nanomedicine.

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