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Nitrogen-doped titanium dioxide: An overview of material design and dimensionality effect over modern applications

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ABSTRACT

TiO_2 material has gained attention as the most studied semiconductor material for photocatalytic purposes, including their use in devices for clean energy production, such as solar cells and water splitting systems. However, the wide band gap of this material limits applications to UV light, which also confines the use of solar irradiation as the energy source. Much research in the last years is showing the ability of N doping into TiO_2 to promote light absorption in the visible range but, to date, it is still controversy if this doping is beneficial to the photocatalytic process, as well as the synthetic methods are not well stabilized yet. Then, this paper summarizes the recent advancement in the structural design perspective of N-doped TiO_2 photocatalyst, in a critical analysis of its application for environmental purposes. We reported the dimensionality effect associated with modified N-doped TiO_2 structure for its characteristics properties and photocatalytic performance; counting more specifically its charge transportation, surface area, adhesion, reflection and absorption properties. A concise view of the doping effect over morphology in 0, 1, 2 and 3-dimensional ranges was provided, in order to understand which effects are also occurring on the materials besides the photocatalytic response. Furthermore, selected recent and significant advances in the area of renewable energy applications for modified N-doped TiO_2 were assessed with the particular importance given towards the electricity generation by dye-sensitized solar cells and lithium-ion batteries rechargeable for electric energy storage.

Contents

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1. Introduction

1.1. Opening of the review

In recent years, the assembly of design principles, synthesis and new applications of N-doped TiO_2 material has remained a topic of intense interest due the increased light absorption, which could allow a more efficient photoactivation by solar light [1–4]. However, literature still has many controversies about the application of this material, as well as a large number of synthetic methods, were reported. Then, it is still a challenge state to opt the best options to produce these materials and how these methods influence in other properties, such as morphology. Then this review summarizes the variety of different structure dimensionality obtained by such methods, which is one of the most effective approaches to applying the unique properties of cited materials in practical applications. The easy preparation of these semiconductors materials may endow with various structural properties regarding their dimensional classification by an array of physical and chemical methods, greatly extending the arsenal of TiO_2 materials for most common application, such as in mechanical energy harvesting using inertial energy harvesting and kinematic energy for applications such as DSSc and Lithium-ion batteries. The information collected in this review discusses the fundamental and critical aspects of structure design and dimensionality for N-doped TiO_2 materials having a high specific surface area, looking for the current applications and challenges associated by emphasizing concepts of its physics and chemistry. This review paper mainly focuses on highlighting and summarizing various structures dimensionality of N-doped TiO_2, in an attempt to organize the information regarding the structure design of N-doped TiO_2 with their properties, synthetic methods, and applications.

The development of photocatalyst using semiconductor nanoparticles has been the subject of considerable attention in the recent era, because of its obvious applications for a broad range of research areas, including current and potential applications such as electronic devices, sensors, energy-related fields and environmental problems [5–9]. Since the breakthrough of water splitting reported by Fujishima and Honda in 1972 [10], extensive and intensive research has been carried out in the investigation of photocatalytic properties of certain materials

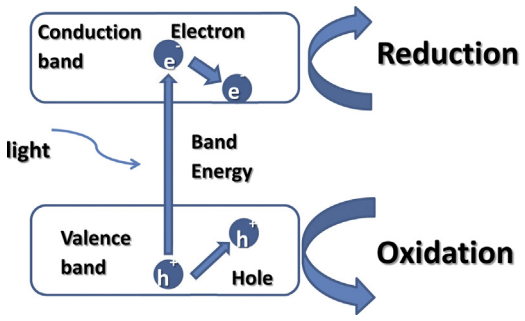

Fig. 1. Schematic representations of photogenerated electron and hole formation upon irradiation of UV light on TiO_2.

to convert abundant, long lasting, and clean solar energy into another form of energy such as chemical energy. In this regard, the under-investigated photocatalysts were subjected to perform oxidation/reduction process for the generation of hydrocarbons [11] and hydrogen [10,12–15] (i.e. beneficial for energy related field) and for the removal of pollutant and bacteria from the air, in water and wall surfaces [16–37]. In broad terms, photocatalytic reactions are divided into two classes; (i) catalyzed photoreaction and (ii) sensitized photoreaction, depending on the approach of initial photoexcitation process. In catalyzed photoreaction, the initial photoexcitation step took place on the catalyst surface as a consequence of electron and/or energy transfer into ground state molecule. In the second case, the adsorbent molecules (e.g. dye molecule) underwent photo-excitation and then interact with ground state photocatalyst [38].

TiO_2, as a first generation material, has the strong oxidizing ability and has been most extensively studied for many applications [28,39–43] such as disposition of contaminants in aqueous and atmospheric ecosystems, super-hydrophilicity [44], and decomposition of organic pollutants [30,31]. These characteristics applications are related due to its appropriate properties namely; chemical stability, long durability, nontoxicity, low cost, and transparency to visible light [28,39–43]. The basic principle of photocatalysis process is started with the formation of photogenerated charge carriers, and namely h^+–e^- pairs upon the absorption of ultraviolet (UV) light (in the case of TiO_2 due to the high band gap), as shown in Fig. 1 [5,7,24,45–47]. The photogenerated charge carriers (h^+–e^- pairs) recombined quickly after irradiation of UV light, which generated heat. Therefore, a few of the photo-generated charge carriers become available for the initiation of photo redox reactions. The efficiency of photocatalytic processes depends upon the lifetime of photo-generated charge carriers and the time scale of interfacial electron transfer. The photo-generated holes diffused on the surface of TiO_2 and, interacted with adsorbed water molecules and/or other compounds i.e. hydroxyl groups. As a result, hydroxyl radicals ($^{\bullet}OH$) [7]) were produced, which alongside photogenerated holes oxidized nearby organic molecules on the surface of TiO_2 photocatalyst. In the meantime, electrons from conduction band participated in reduction processes and reacted with molecular oxygen yielding in superoxide radical anions ($O^{2\bullet-}$). Two basic principles accounting for the conversion of light energy into a useful generation of charge carriers are electron photogeneration/recombination and electron transfer on the surface of a photocatalyst. Therefore, major issues concerned for photocatalysis includes; how to increase the efficiency of charge carriers separation/transport in semiconductor nanoparticles?

Another important factor which accounts for the application of TiO_2 is the super hydrophilic nature of the TiO_2 surface and originated from the chemical confrontation of changes on the surface. It was found that the contact angle under the UV-light irradiation is reduced to less than 5° in the case of TiO_2 [44,47]. Therefore, the