Synthesis and Applications of TiO_2/ZnO Hybrid Nanostructures by ZnO Deposition on TiO_2 Nanotubes using Electrochemical Processes

P.J. Navarro-Gázquez[1], M.J. Muñoz-Portero[1], E. Blasco-Tamarit[1], R. Sánchez-Tovar[2], J. García-Antón[1,*]

[1]*Instituto Universitario de Seguridad Industrial, Radiofísica y Medioambiental (ISIRYM). Universitat Politècnica de València. Camino de Vera s/n, 46022 Valencia, Spain.*

[2]*Departamento de Ingeniería Química, Universitat de Valencia, Av. de las Universitats, s/n, 46100 Burjassot, Spain.*

**Tel. 34-96-387 76 32, Fax. 34-96-387 76 39, e-mail: jgarciaa@iqn.upv.es*

Abstract

In recent years, TiO_2/ZnO hybrid nanostructures have been attracting the interest of the scientific community due to their excellent photoelectrochemical properties. The main advantage of TiO_2/ZnO hybrid nanostructures over other photocatalysts based on semiconductor materials lies in their ability to form heterojunctions in which the valence and conduction bands of both semiconductors are intercalated. This factor produces a decrease in the band gap and the recombination rate and an increase in the light absorption range. The aim of this review is to perform a revision of the main methods to synthesise TiO_2/ZnO hybrid nanostructures by ZnO deposition on TiO_2 nanotubes using electrochemical processes. Electrochemical synthesis methods provide an easy, fast, and highly efficient route to carry out the synthesis of nanostructures such as nanowires,

nanorods, nanotubes, etc. They allow us to control the stoichiometry, thickness and structure mainly by controlling the voltage, time, temperature, composition of the electrolyte and concentration of monomers. In addition, a study of the most promising applications for TiO_2/ZnO hybrid nanostructures has been carried out. In this review, the applications of dye-sensitised solar cell, photoelectrocatalytic degradation of organic compounds, photoelectrochemical water splitting, gas sensors and lithium-ion batteries have been highlighted.

Keywords: TiO_2/ZnO hybrid nanostructures, titanium dioxide, zinc oxide, electrochemical anodization, electrodeposition process.

1. Introduction

In recent years, semiconductor nanomaterials have attracted the interest of researchers due to their unique properties and potential applications. One of the most important properties of most semiconductor nanomaterials is that the transfer of electrons and holes is controlled by the phenomenon of quantum confinement, while the transport of photons is closely related to the size and morphology of their surface. The quantum confinement effects allow to modify the structure of electronic bands and increase the efficiency in the transport of photogenerated electrons and holes (Adams et al., 2003; Alivisatos, 1996; Roduner, 2006). In addition, the high surface area to volume ratio of nanomaterials increases the surface reaction sites, allowing them to improve their catalytic properties. The specific surface area and the surface/volume ratio increase as the size of the nanostructure decreases (Valden et al., 1998). Increasing the specific surface area is beneficial to some applications such as catalysis, photocatalysis and electronic devices (Acar et al., 2016; Chu et al., 2012; Kuchibhatla et al., 2007; Soares and Alves, 2018; Zhang and Cao, 2011).

Since Iijima discovered carbon nanotubes in 1991 (Iijima and Ichihashi, 1993), one-dimensional nanomaterials have drawn great attention due to their unique physical and chemical properties. These excellent properties can vary depending on the nanostructure morphology. One-dimensional nanostructures typically consist of nanotubes, nanowires, nanorods and nanobelts, and at least one of their dimensions should be in the 1-100 nm range. Each of them has different geometry, properties and synthesis strategies (Kuchibhatla et al., 2007; Xia et al., 2003). Nanotubes have excellent properties due to the unique combination of their shape, nanosize and functionality (Hidayat et al., 2019; Lin et al., 2013; Mor et al., 2006b).

Over the last years, nanomaterials research has focused on electrical and optoelectronics devices. Semiconductor oxides have been of great interest due to their wide range of electrical and optical properties, which can be explained by the solid-state band theory and by ionic bonding concepts from solid-state chemistry (Banerjee, 2011). The electronic properties of these semiconductor materials depend, mainly, on the nature of the cation-oxygen bonding, which influences the electronic configuration, the coulombic force of the cation-oxygen bond and the delocalization of holes at the edge of the valence band (related to oxygen vacancies) (Banerjee and Chattopadhyay, 2005; Feldheim and Keating, 1998; Klein et al., 1997).

Titanium oxide (TiO_2) is the most popular and prospect photoelectrocatalyst due to its high chemical stability, low toxicity, excellent physical properties and low cost. TiO_2 is a n-type semiconductor generally consisting of two stable crystalline structures, anatase (3.2 eV) and rutile (3.0 eV) (El Ruby Mohamed and Rohani, 2011; Feng et al., 2017; Macak et al., 2007; Maziarz et al., 2016; Ng et al., 2015). TiO_2 nanostructures have a high specific energy density, an abundant availability, a large surface area and a wide band gap that provides them a large number of active sites. The main characteristic of TiO_2 nanostructures is that they can absorb photons when they are irradiated with light of a wavelength whose energy is equal to or greater than its band gap. This phenomenon causes the excitation of electrons from the valence band to the conduction band, generating electron-hole pairs, which improves the photocatalytic activity, electrochemical properties and the gas sensitivity of TiO_2 nanostructures (Banerjee, 2011; El Ruby Mohamed and Rohani, 2011; Nagamine, 2020; H. Wang et al., 2014; Zhang and Cao, 2011). The photon energy absorbed by photocatalysts produces the excitation of electrons up to the conduction band originating holes in the valence band. The photoexcited electrons will induce reduction processes, while the holes originated in the

valence band will cause oxidation processes. Another of the most interesting characteristics of TiO_2 nanostructures is that they have few trap defects in their anatase crystalline phase, so they can be used as photoanodes providing a rapid electron transport, which results in a high photocatalytic performance (El Ruby Mohamed and Rohani, 2011; Kenanakis et al., 2015; Nagamine, 2020; H. Wang et al., 2014; Zhang and Cao, 2011).

In one-dimensional TiO_2 nanostructures, as it also occurs in TiO_2 nanoparticles, the movement of electrons and holes is governed by quantum confinement, and the transport properties related to electrons and photons are affected by the size and geometry of the materials. However, a higher surface area to volume ratio of one-dimensional TiO_2 nanostructures gives them unique physical and chemical properties and higher photoelectrochemical performance in some areas. These properties are closely related to the size of the material on a nanometric scale and the morphology of nanomaterials (Chen and Mao, 2007; M. Yang et al., 2009). So far, a wide variety of one-dimensional TiO_2 nanostructures have been found, such as nanotubes (El Ruby Mohamed and Rohani, 2011; Huang et al., 2013; Indira et al., 2015; M. Wang et al., 2014), nanowires (Banerjee, 2011; Ramgir et al., 2020; D. Wang et al., 2014; X. Wang et al., 2014), nanofibers (Banerjee, 2011; Nagamine, 2020; Zhou et al., 2010), nanorods (Banerjee, 2011; Kuchibhatla et al., 2007; X. Wang et al., 2014; Zhang and Cao, 2011; Zhou et al., 2010), nanobelts (Banerjee, 2011; X. Wang et al., 2014; Zhang and Cao, 2011; Zhou et al., 2010), or nanosponges (Blasco-Tamarit et al., 2018; Guo et al., 2008; Sanchez-Tovar et al., 2013; Sánchez-Tovar et al., 2017, 2015a), among others. However, most research has focused mainly on four categories: nanowires, nanobelts, nanorods and nanotubes (see Figure 1). The first three categories have a solid structure, while nanotubes have a central hole. The nanostructure that has attracted most interest is TiO_2 nanotubes matrices. They are extremely functional materials with a wide range of applications due to their good

semiconducting and biocompatibility properties (El Ruby Mohamed and Rohani, 2011; Huang et al., 2013; Indira et al., 2015; Le and Leu, 2018; X. Wang et al., 2014).

Currently, TiO_2 nanostructures are showing great progress in applications such as dye-sensitised (Mor et al., 2006a; Tsvetkov et al., 2020; H. Wang et al., 2014; Zhang and Cao, 2011), sensor devices (Drunka et al., 2019; Huang et al., 2013; Maziarz et al., 2016), degradation of organic pollutants (Abellán et al., 2009; Gaya and Abdullah, 2008; Hoffmann et al., 1995), Lithium-ion batteries (Farooq et al., 2020; X. Wang et al., 2014; Yu et al., 2017) and photoelectrocatalytic water splitting (Ni et al., 2007; Palmas et al., 2010; Sánchez-Tovar et al., 2017, 2015a). For these applications, the performance of TiO_2 nanostructures depends, mostly, on the process of optical absorption of incident photons and, consequently, on the photogeneration of electron-hole pairs. The electron-hole pairs are disseminated across the entire surface of the nanostructures and they are responsible for starting chains of photoelectrochemical reactions.

However, TiO_2 has several limitations for contemporary applications. It has a large band gap (~3.2 eV) —which limits some photocatalytic reactions—, low photocatalytic activity under visible light, a large interfacial area that produces a poor charge transport and single-phase and nanoscale characteristics —which induces rapid recombination of photoexcited charge carriers (Maziarz et al., 2016; Tian et al., 2014) —.

In order to overcome these limitations, research has focused mainly on the doping of TiO_2 nanostructures (Bonatto et al., 2020; El Ruby Mohamed and Rohani, 2011; Farooq et al., 2020; Lai et al., 2010; Sánchez-Tovar et al., 2017; Yang et al., 2017b) and the synthesis of hybrid nanostructures (Feng et al., 2017; Kusior et al., 2019; Liao et al., 2018; Lin et al., 2013; Liu et al., 2014; Oliveira et al., 2010; Prabakaran et al., 2019; Reddy et al., 2020; Sun et al., 2018; Yuan et al., 2017). Although in previous decades doping of TiO_2

nanostructures has seized practically all the attention, currently, research related to the synthesis of TiO_2 hybrid nanomaterials using metal oxides is gaining importance. TiO_2 hybrid nanomaterials have been obtained with a large variety of metal oxides, such as tin oxide (SnO_2) (Kutuzova et al., 2020; Sharma et al., 2021), tungsten oxide (WO_3) (Odhiambo et al., 2020; Soares and Alves, 2018), zinc oxide (ZnO) (Hashem and Abdal-hay, 2021; Hashemi et al., 2020; Q. Jiang et al., 2022; Sánchez-Tovar et al., 2020; M. Wang et al., 2013), silicon oxide (SiO_2) (Liu et al., 2013; Mendoza et al., 2014), copper (II) oxide (CuO) (Kianfar and Arayesh, 2019; Kubiak et al., 2020; Li et al., 2017), etc. TiO_2/ZnO hybrid nanostructures have been selected as one of the most promising due to the high reactivity potential of TiO_2 and the high electron mobility of ZnO.

ZnO nanostructures have attracted considerable interest due to their potential energy and environmental applications (Batista-Grau et al., 2020; Drunka et al., 2019; Samadipakchin et al., 2017; Zaitsev et al., 2019). The devices that use ZnO as photoelectrodes can get high conversion efficiency of solar energy to electrical energy. In addition, ZnO nanostructures have chemical and thermal stability, non-toxicity, low cost, a direct band gap around 3.4 eV and large excitation binding energy (60 meV). For these reasons, they have been widely used in photoelectrocatalytic reactions (Batista-Grau et al., 2020; Drunka et al., 2019; Samadipakchin et al., 2017; H. Y. Yang et al., 2009). Compared to TiO_2, ZnO has a greater oxidization capacity of photogenerated holes, better electrical transport properties and greater electron mobility (Xu et al., 2017).

The main advantage of TiO_2/ZnO hybrid nanostructures is that the electrons and holes photogenerated when irradiating the nanostructures with a wavelength whose energy is equal to or greater than their band gap can move between the valence and conduction bands of both semiconductors. The photoexcited electrons from the conduction band of

ZnO are transferred to the conduction band of TiO_2, and the holes from the valence band of TiO_2 are transferred to the valence band of ZnO, which reduces the recombination rate of load carriers (Hernández et al., 2015; Ng et al., 2018). This phenomenon is carried out because ZnO has a similar band gap (3.4 eV) to TiO_2 (3.2 eV). Although ZnO stability in electrochemical reactions under ultraviolet (UV) light irradiation is very limited, when forming TiO_2/ZnO hybrid nanostructures, TiO_2 acts as a protective matrix, substantially increasing stability (Hernández et al., 2015; Liao et al., 2018; Liu et al., 2014). Furthermore, since ZnO has a more negative conduction band edge (–0.32 V vs SHE (Lin et al., 2016)) than TiO_2 (0.27 V vs SHE (Lu et al., 2012)), the photoelectrochemical activity of the nanostructures under UV irradiation improves when TiO_2/ZnO hybrid nanostructures are formed (Lin et al., 2013).

Over the years, numerous synthesis methods for TiO_2/ZnO hybrid nanostructures have been developed, such as hydrothermal methods (Feng et al., 2017; Xu et al., 2017), sol-gel (Indora et al., 2020; Tsvetkov et al., 2020), spin coating (Marimuthu and Anandhan, 2017), thermal decomposition (Liao et al., 2018), atomic layer deposition (ALD) (Yang et al., 2017b, 2017a) and electrodeposition (Benkara and Zerkout, 2010; Sánchez-Tovar et al., 2020). Most of the methods used to form TiO_2/ZnO hybrid nanostructures involve a previous step in which a TiO_2 nanostructure is formed, mainly TiO_2 nanotubes. Therefore, in this work, in addition to the discussion of the synthesis methods of TiO_2/ZnO hybrid nanostructures, a small compilation of the main methods of synthesis of TiO_2 nanotubes was made focusing on the electrochemical anodization of Ti.

2. Synthesis of TiO_2 nanotubes

The formation of TiO_2 nanostructures increases the surface area of TiO_2 photoelectrocatalysts, improves their electronic properties and controls its physical and

chemical behaviour. Furthermore, TiO_2 nanostructures contribute to improve the reaction/interaction between a device and the surrounding environment making the system more efficient and forming new reaction pathways (Roy et al., 2011). The photochemical and surface properties of TiO_2 photocatalysts are highly dependent on the nanoscale and their specific surface area, which is related to the size and shape of the nanostructures (Banerjee, 2011).

The photoelectrocatalytic activity of TiO_2 is mainly related to the size, shape and number of defects of the nanostructures. For this reason, the optimization of morphology and crystallinity has been studied over the years and a great variety of nanostructures has been developed. The most studied and reported nanostructures are clearly the TiO_2 nanotubes. The tubular configuration provides unidirectional electrical channels that improve the charge transport and increase the surface area, without affecting the geometric surface of TiO_2 nanostructures (Hernández et al., 2015).

TiO_2 nanotubes can be obtained mainly from electrochemical deposition (Lai et al., 2010; Michalcik et al., 2012), electrochemical anodization (Indira et al., 2015; Lai et al., 2009; Le and Leu, 2018; Macák et al., 2005; Zhou et al., 2014) and template-assisted methods such as sol-gel techniques (Archana et al., 2019; Indora et al., 2020; Kenanakis et al., 2015; Tsvetkov et al., 2020), hydro/solvothermal methods (Kasuga et al., 1999; Tian et al., 2003; Yao et al., 2003) and atomic layer deposition (ALD) (Yang et al., 2017b, 2017a). The methods that involve the use of templates require a subsequent compaction process on the surface of a conductive electrode, which implies that nanotubes have an arbitrary orientation with respect to the electrode, thus eliminating the advantages of having one-dimensional directionality nanostructures. However, the electrochemical anodization method makes it possible to form a matrix of TiO_2 nanotubes perpendicularly

aligned to the substrate surface with a well-defined and controllable tube length (Huang et al., 2013; Indira et al., 2015; Sánchez-Tovar et al., 2015a).

Electrochemical synthesis methods are based on controlled oxidation and reduction reactions. They provide an easy, fast, and highly efficient route to carry out the synthesis of nanostructures such as nanowires, nanorods, nanotubes, etc (Topo, 2013). Electrochemical methods allow to control the stoichiometry, thickness and structure of the formed films mainly controlling the voltage, time, the composition of the electrolyte and the concentration of monomers. The manipulation of these variables provides a wide range of morphologies and growth rates, giving excellent control over the morphological properties of photoelectrodes. Moreover, precise control over the growth process of nanostructures can be obtained by monitoring the potential or current during the synthesis process (Choi et al., 2010; Ostojic et al., 2017; Pantelis and Tsiourva, 2017). The main advantages of electrochemical synthesis methods compared to other methods such as the hydrothermal method, sol-gel or atomic layer deposition is that the synthesis can be carried out easily, at low cost, with high purity and at low temperatures and pressures. In addition, they have the advantage that the nanostructured material grows directly on a conductive substrate, which is very favourable for device assembly (Topo, 2013; Yoon et al., 2016). Furthermore, since a wide range of materials such as metals, oxides, or hydroxides, among others, can be synthesised by electrochemical methods, the strategies developed to obtain a certain morphology could be extrapolated to various materials (Choi et al., 2010).

In recent years, numerous methods to form TiO_2 nanotubes have been developed due to the extraordinary and novel properties that these nanostructures exhibit. Probably, the first method to produce TiO_2 nanotubes was the electrochemical deposition method

(Hoyer, 1996). In that research, TiO_2 nanotubes were electrodeposited into an ordered alumina template (Al_2O_3 layer) using an electrolyte formed by titanium (III) chloride ($TiCl_3$) with a potential of 0.4 V vs silver/silver Chloride (Ag/AgCl). The nanotubes formed had a length of 8 μm with an inner diameter between 50 and 70 nm and a wall thickness of about 25 nm (Hoyer, 1996). This technique is based on applying an electrical potential that makes the addition of the metallic cations contained in an aqueous solution to a conductive substrate possible. Although it is not very common to use this method to synthesise TiO_2 nanotubes, some publications can be found in literature. TiO_2 nanotubes can also be formed by one-step electrodeposition without using metal titanium (Ti) substrates or templates, carrying out an electrochemical deposition process on fluorine-doped tin oxide (FTO) with an aqueous solution composed of ammonium hexafluorotitanate ($(NH_4)_2TiF_6$) and boric acid (HBO_3) at a constant potential of –0.8 V vs Ag/AgCl (4 M potassium chloride (KCl)) at 90 °C for 30 min (Chu et al., 2012).

Later on, other techniques involving the use of templates have also been reported such as sol-gel techniques, hydro/solvothermal methods and atomic layer deposition (ALD). Most of the processes that involve the use of these techniques employ acid-catalysed hydrolysis reactions of titanium alkoxide precursors followed by condensation reactions (Roy et al., 2011). For example, TiO_2 nanotubes can be prepared with a sol-gel method combined with a hydrothermal process. These methods usually use high temperature, high pressure and aqueous catalyst solutions (Banerjee, 2011; Roy et al., 2011; Tsvetkov et al., 2020; Zhang et al., 2002). First, a mixture with the precursor material —such as titanium isopropoxide, for example— is made. Then, a hydrolysis step is carried out and the final solution is evaporated to get a dry gel mixture. The nanostructures are treated with NaOH solution in an autoclave and subsequently an acid treatment is performed. Finally, TiO_2 nanotubes are obtained by rolling of the nanolayer sheets into tubes. The

amount, length and size of the synthesised nanotubes depend on the specific conditions in which the reaction is carried out (Cheng et al., 2016; Tsvetkov et al., 2020).

Another well stablished method to synthesise TiO_2 nanotubes is the ALD method. A template surface —such as a carbon nanotubes template— is coated with one atomic layer over another through alternating cycles of exposure to a titania precursor —such as titanium isopropoxide— followed by hydrolysis and purging steps. It allows the formation of vertically aligned rod or nanotubular structures on the surface of the substrate. However, it sometimes involves a critical step of template removal (Roy et al., 2011; Yang et al., 2017a, 2017b).

With these synthesis methods, single tubes or tube clusters that require a subsequent compaction step are formed, resulting in arrays of nanotubes with arbitrary orientation (Roy et al., 2011). In order to solve these problems, electrochemical anodization process is used to coat the titanium surface with a dense, well-defined and controlled length nanotube layer, without the need to perform a subsequent compaction step on a conductive substrate. This synthesis method makes it possible to take full advantage of the benefits of one-dimensional directionality nanostructures. In addition, it is an extremely versatile and easy to scale structuring process (Paramasivam et al., 2012; Roy et al., 2011).

Of all the methods, special attention is given to the direct oxidation of Ti metal using an oxidizing agent through a conventional electrochemical anodization, which implies that the synthesis is developed at low cost. This method has the inherent advantage of forming TiO_2 nanostructures directly on titanium substrates, so they do not need to be compacted or sintered at a later stage. Electrochemical anodization makes it possible to form self-ordered TiO_2 nanomaterials on titanium substrates. It is a very useful method to form a

wide variety of one-dimensional TiO_2 nanostructures such as nanoporous or nanotubular structures.

2.1. Electrochemical anodization for the formation of self-organized TiO_2 nanotubes

Although a large number of nanostructures can be formed by electrochemical anodization of metal Ti, such as nanowires (X. Wang et al., 2014), nanotubes (Indira et al., 2015), nanoflowers (Kusior et al., 2015), nanosponges (Sanchez-Tovar et al., 2013), etc., TiO_2 nanotubes are the nanostructures that have attracted the most attention. Zwilling et al. (1999) developed in 1999 the first electrochemical anodization process for the formation of self-ordered TiO_2 nanostructures. TiO_2 nanotubes were formed by electrochemical anodization at room temperature and using a fluoride electrolyte. However, the thickness of the layers obtained exceeded 500 nm and the aspect ratio was significantly low.

Fluoride ions attack the compact titanium dioxide layer dissolving the formed TiO_2 and producing pores, cracks, or tubes, which form the TiO_2 nanostructure. Different structures of titanium oxide such as compact oxide plane or a highly self-organizing nanotube layer can be obtained by controlling the electrochemical anodization parameters (temperature, potential, electrolyte species, viscosity, electrolyte pH, aqueous or organic electrolytes, etc.) (Huang et al., 2013). The electrochemical anodization generally consists of 3 stages (Figure 2). In the first stage, there is an increase in resistance (decrease in current density) caused by the growth of a TiO_2 layer on the metallic titanium substrate. In the second stage, there is an increase in current density caused by a local thinning of the TiO_2 layer. This fact occurs because fluorides react with TiO_2 originating $[TiF_6]^{2-}$ complex, which is

dissolved in the medium. Finally, in the third stage, the equilibrium between the formation and the dissolution of TiO_2 is reached (Ghicov and Schmuki, 2009).

Different concentrations of fluorides result in different anodization behaviours. On the one hand, if fluoride content is too low, only a TiO_2 compact layer is formed. This is because there are not enough fluorides to attack titanium dioxide. On the other hand, when the fluoride concentration is too high, there is no oxide formation because all TiO_2 react immediately with the fluorides forming $[TiF_6]^{2-}$. For this reason, the fluoride concentration must be at an intermediate value (Qin et al., 2021b; Roy et al., 2011).

After the research carried out by Zwilling et al. (1999), a multitude of procedures have been developed to find the optimal electrolyte and the experimental parameters that allow to get high quality self-organizing nanostructures efficiently. At first, the most used electrolyte for the TiO_2 nanotubes formation by electrochemical anodization was a hydrofluoric acid solution (HF) (Mor et al., 2006b). Well-aligned TiO_2 nanotube arrays can be obtained using an aqueous HF electrolyte with a concentration of 0.5 wt.% and potentials between 10 and 20 V for 20 min at room temperature. The lower the HF concentration is, the higher the voltage will be to form tubular nanostructures. In these conditions, the mean diameter of the tube increases as the potential increases (Gong et al., 2001; Mor et al., 2003). Furthermore, it has been shown that, when using an electrolyte formed by 0.5 wt.% HF + acetic acid in 7:1 ratio with a potential of 10 V, the wall thickness and the nanotubes length decrease when increasing the anodization temperature (Mor et al., 2005). Other fluorinated compounds, such as sodium fluoride (NaF), have also been studied afterwards. It is possible to form TiO_2 nanotubes with a well-organized homogeneous porous structure using an electrolyte composed of 1M

sodium sulphate (Na_2SO_4) with different amounts of NaF (0.5 - 1 wt.%) and applying a potential of 20 V for at least 2 hours (MacAk et al., 2005).

The control of the length, pore size and wall thickness of nanotubes mainly depends on the electrolyte. Currently, the morphology of TiO_2 nanotubes can be easily controlled by adjusting the anodization conditions and using novel electrolytes (Prakasam et al., 2007; Wang et al., 2009). In a research carried out by Prakasam et al. (2007), the influence of anodization parameters on the dimensions of nanotubes was analysed. For this purpose, an electrolyte composed of ethylene glycol, water and ammonium fluoride (NH_4F) were used. The anodization process was carried out by modifying the NH_4F concentration (0.1 - 0.5 wt.%), water concentration (1-3 vol.%), potential (20-80 V) and time (4 - 96 h) while the anodization temperature was kept constant (22 °C). The results showed the formation of highly ordered nanotube arrays whose dimensions can be easily adjusted from the anodization parameters. For a potential of 60 V and an anodization time of 17 h, it was observed (i) an increase in the length of the nanotubes when the concentration of NH_4F increased from 0.1 to 0.3 wt.% and (ii) an increase in the length of the nanotubes for NH_4F concentrations lower than 0.3 wt.% by increasing the water concentration from 0 to 2 vol.%. In addition, for an anodization time of 17 h and concentrations of 0.3 wt.% NH_4F and 2 vol.% water, an increase in the length of the nanotubes from 5 to 165 μm was observed when the potential increased from 20 to 60 V, respectively. For these conditions, an increase in both the internal and the external diameter was also observed. Finally, the anodization time was altered between 4 and 96 h. The results showed that the length of the nanotubes increases as the anodization time increases, obtaining a length of 360 μm for the anodized nanotubes during 96 h. The use of new electrolytes with an organic base makes it possible to significantly increase the growth rate of the nanotubes with respect to that obtained with amide-based electrolytes and aqueous solutions.

One of the most important aspects of photocatalysts based on TiO_2 nanotubes is the pore diameter. A decrease in the pore diameter of the nanotubes provides a greater number of active sites and an increase in photocatalytic performance. The pore diameter of TiO_2 nanotubes is mainly influenced by the applied potential and the electrolyte composition (fluoride concentration, amount of water, viscosity, acidity, etc.). Although the pore diameter of TiO_2 nanotubes does not depend solely on a single parameter, since it is necessary to optimize all of them, it generally decreases as the applied potential and water content decrease and the fluoride concentration increases (Mansoorianfar et al., 2021; Mercado et al., 2019; Qin et al., 2021a, 2021b, 2015). According to the bubble mould theory, a high current density will reduce a large amount of oxygen ions pressurizing the oxide layer and generating nanotubes of larger diameters, while cavities cannot grow normally with an excessively low current density due to the lack of sufficient oxygen molecules in the oxide layer (Mansoorianfar et al., 2021).

Besides studying the influence of electrolyte composition, potential and time, parameters such as hydrodynamic conditions during the anodization process have also been recently studied. This technique is relatively novel and it consists of spinning the working electrode around its own axis using a rotating system. Highly ordered TiO_2 nanotube arrays can be synthesised by anodization under hydrodynamic conditions using electrolytes composed of ethylene glycol, water (1 M) and NH_4F (0.01 - 0.5 M). The potential used is 55 V and the anodization time can be 15 or 30 min. The rotation speed of the working electrodes can be adjusted based on the Reynolds (Re) number. With hydrodynamic conditions, it is possible to obtain much more defined nanotubes than under static conditions. This is because the flow conditions are much better under these conditions than under magnetic stirring conditions. Furthermore, under static conditions, nanotubes have an initiation layer on their top limiting the efficiency of the photocatalyst

due to the reflection losses. However, under hydrodynamic conditions, the initiation layer is removed. As the Re number increases, the tube entrances become more visible and defined and the diameter of nanotubes increases. This system makes it possible to design both the top of the tubes and their length and to remove unwanted top layers. The elimination of the initiation layer of nanotubes results in an increase in their efficiency for photoelectrochemical applications (Sánchez-Tovar et al., 2015b, 2012).

Although ethylene glycol is the most widely used compound to form TiO_2 nanotubes on an organic basis, other compounds such as glycerol have also been used. It is possible to synthesise TiO_2 nanotubes using electrolytes composed of glycerol/water (60:40 vol.%) and NH_4F, both under static and hydrodynamic conditions. In these conditions, nanostructures with nanotubes or nanosponges morphology could be synthesised by modifying the parameters of the anodization process (Sánchez-Tovar et al., 2017, 2015a, 2013). Figure 3 shows a summary of the morphology obtained as a function of the anodization conditions at room temperature in electrolytes composed of glycerol/water (60:40 vol.%) (Sánchez-Tovar et al., 2013).

Once the anodization process is finished, TiO_2 nanostructures usually present an amorphous structure regardless of the anodization conditions used. Therefore, it is necessary to carry out a heat treatment to convert their amorphous structure into a crystalline structure (Asgari et al., 2017; Blasco-Tamarit et al., 2018; Fakharuddin et al., 2015; Indira et al., 2015; Sánchez-Tovar et al., 2017, 2015a, 2015a; Sivaprakash and Narayanan, 2020; Zhou et al., 2014). However, it is also possible to synthesise crystalline TiO_2 nanostructures by electrochemical anodization, without the need to perform a subsequent heat treatment. The main parameters that affect the crystallinity of the as-anodized TiO_2 nanostructures are the applied potential, anodization time, fluoride

concentration and amount of water added. Allam and Grimes (2009) studied the influence of the potential and electrolyte composition on the crystallinity of TiO_2 nanotubes synthesised by electrochemical anodization (Figure 4). An increase in applied voltage improved the crystallinity of as-anodized TiO_2 samples, using electrolytes composed of ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TetEG) or polyethylene glycol 400 (PEG) in combination with 0.2 M NH_4F, 0.05 M H_2SO_4 and different percentages of water for 20 h. The amount of added water plays a critical role on the crystallinity and morphology of the TiO_2 films formed by electrochemical anodization. A small amount of water can help the formation of crystalline anodic TiO_2 films, while a too high amount of water leads to the formation of amorphous anodic TiO_2 films (Allam and Grimes, 2009; Su et al., 2013; Tsuji et al., 2014).

Crystallinity has an influence on the photoelectrochemical performance and the light adsorption of photocatalysts (Duarte et al., 2020; Li et al., 2009; Mercado et al., 2019; Tsui et al., 2013; Tsvetkov et al., 2020). Figure 5 shows the photoluminescence of TiO_2 nanostructures as a function of the annealing temperature (Yu and Wang, 2010). The crystalline phase can be controlled with the annealing temperature. The most suitable crystalline phases to carry out photoelectrochemical applications are the anatase and rutile phases. When carrying out a heat treatment between 300 and 600 °C, the anatase phase is mainly observed. In this temperature range, the crystallinity of nanostructures and the size of the crystallites formed increase by increasing the annealing temperature from 300 to 600 °C. At a temperature of 600 °C, the three crystalline phases of TiO_2 are present: rutile, anatase and brookite, although the brookite phase appears in a very low proportion. The transformation of the anatase phase into the rutile phase takes place in temperatures between 600 and 800 °C. The anatase phase decreases and the rutile and brookite phases

increase as the annealing temperature increases. From 700 °C on, most of the anatase phase is transformed into the rutile phase. For annealing temperatures above 800 °C, the TiO_2 nanostructures mainly show the brookite phase (Allen et al., 2018; Duarte et al., 2020; Yu and Wang, 2010). Table 1 shows some examples of the main parameters used to synthesise TiO_2 nanotubes by electrochemical anodization of Ti, according to the research carried out in the last years.

3. Synthesis of TiO_2/ZnO hybrid nanostructures

The photocatalytic activity of TiO_2 nanostructures under visible light irradiation is limited due to its wide band gap (3.2 eV for anatase phase, $\lambda = 390$ nm and 3.0 eV for rutile phase, $\lambda = 415$ nm) (Miyoshi et al., 2018; Reyes-Coronado et al., 2008). The photoelectrochemical performance depends mainly on the process of optical absorption of photons, which generates electron-hole pairs that will initiate chains in photochemical reactions. In general, metal oxide photocatalysts are not photocatalytically excited in the visible range because they have wide band gaps, such as TiO_2 and ZnO. Since the ultraviolet light represents only a 7 % of the solar spectrum, it is necessary to reduce the band gap of the photocatalysts to extend the light absorption range of photocatalysts and thus improve their photocatalytic activity. However, reducing the band gap causes an increase in recombination processes and, therefore, a decrease in the photoelectrochemical efficiency (Hernández et al., 2015; Liao et al., 2018; Lin et al., 2013; Lü et al., 2010).

Physical and chemical properties of TiO_2/ZnO hybrid nanostructures are better than the individual properties of both semiconductors. The electron mobility of ZnO (205 - 300 $cm^2 \cdot V \cdot s^{-1}$) is higher than the one of TiO_2 (0.1 - 4 $cm^2 \cdot V \cdot s^{-1}$). Therefore, the conductivity of TiO_2 nanostructures improves considerably when ZnO is introduced inside the TiO_2

matrix. Furthermore, both TiO_2 and ZnO have the ability to absorb light of a specific wavelength, which causes the promotion of electrons from their valence bands to their conduction bands, generating electron-hole pairs (Lü et al., 2010; Ramgir et al., 2020).

One of the most negative aspects of using ZnO for photoelectrochemical applications is its low stability. However, the stability of the photocatalyst can increase considerably by forming TiO_2/ZnO hybrid nanostructures because TiO_2 acts as a protective matrix (Liao et al., 2018). In addition, the electronic states of TiO_2 and ZnO change when they are combined, obtaining a better separation of charges. The recombination processes of electron-hole pairs are reduced due to the fact that an exchange of electrons and holes occurs between the conduction (CB) and valence (VB) bands of ZnO and TiO_2. The photogenerated electrons from the CB of ZnO are transferred to the CB of TiO_2, while the photogenerated holes from the VB of TiO_2 are transferred to the VB of ZnO (Figure 6). The electron transport process results in a reduction in the charge recombination, increasing the concentration of free electrons in the conduction band and the holes in the valence band (Hernández et al., 2015; Liao et al., 2018; Lin et al., 2013; Lü et al., 2010; Zhang et al., 2008).

3.1. Interfacial structure of TiO_2/ZnO hybrid nanostructures

TiO_2/ZnO heterojunctions have attracted considerable interest in photocatalytic and solar cell applications due to their improved structural and optical properties. This is because the heterojunctions formed at the interface of TiO_2 and ZnO increase the separation of photogenerated electron-hole pairs, thus decreasing recombination processes and increasing photoinduced charge transfer at the semiconductor/electrolyte interface (X. Jiang et al., 2022). The synthesis of TiO_2/ZnO hybrid nanostructures can generate the formation of Zn-O-Ti heterojunctions between the TiO_2 and ZnO interface, producing an

increase in the light absorption range, which leads to a decrease in the band gap of the photocatalysts. The introduction of one crystalline phase in another one influences the electronic structure of the hybrid material. The energy levels of the doping material can enhance the formation of new energy levels close to the valence and conduction bands of the original material, which might reduce its band gap. This phenomenon can occur in the TiO_2/ZnO hybrid nanostructures due to the proximity of the valence and conduction bands of both semiconductors, generating new energy levels that would reduce the band gap of the TiO_2/ZnO hybrid nanostructures, compared to pure TiO_2 and ZnO (Giannakopoulou et al., 2014; Prasannalakshmi and Shanmugam, 2017). In conclusion, the formation of TiO_2/ZnO hybrid nanostructures can improve the response to visible light, charge transfer and charge separation, compared with pure TiO_2, and reduce the photocorrosion of ZnO, compared to pure ZnO (Arin et al., 2013; Chen et al., 2018; Q. Jiang et al., 2022; Ma et al., 2018).

The similarity of energy between the valence and conduction bands of ZnO and TiO_2 allows to transfer photogenerated electrons and holes in the TiO_2/ZnO heterojunction. The formation of TiO_2/ZnO heterojunctions produces structural defects that reduce the band gap of the photocatalysts, thus increasing the useful life of the photogenerated electrons and holes and reducing the chances of recombination. In addition, a red shift of the absorption wave also occurs when forming TiO_2/ZnO hybrid nanostructures, which may be related to the formation of heterojunctions at the TiO_2/ZnO interface (Bai et al., 2021). For example, in Dye-sensitised solar cell (DSSC) systems, the photocurrent density depends mainly on light absorption, photoelectron injection, and charge transport. Lou et al. (2013) reported that the addition of a TiO_2 passivation layer on the surface of ZnO nanocrystal photocatalysts increased the recombination resistance and the lifetime of photoexcited electrons, compared to pure ZnO nanocrystals. The connections between

TiO_2 and ZnO increased the mobility of electrons, which improved the transport of photoelectrons to the external electrical circuit, resulting in a lower resistance to charge transfer and a higher photocurrent density. The photocurrent density of the cell increases as the connections between the valence and conduction bands at the TiO_2/ZnO interface increase. The increase of the TiO_2 nanoparticles in the ZnO matrix produced an increase in the photocurrent density until reaching an optimal value from which it was not possible to increase the number of heterojunctions in the TiO_2/ZnO interface. An excess of TiO_2 nanoparticles led to a decrease in the photocurrent density and energy conversion efficiency.

In an investigation carried out by Li et al. (2020), photoanodes of ZnO microspheres passivated with TiO_2 were formed. In this work, the influence of the TiO_2 passivation layer and its thickness on photovoltaic performance was studied. The results showed that the effects related to light harvesting and electron collection could be improved by adjusting the thickness of the TiO_2 passivation layer. The formation of hybrid microspheres of TiO_2/ZnO allowed to increase the absorbance and the efficiency in the capture of light and to reduce the recombination processes. The combination of TiO_2 and ZnO made it possible to improve the light capture capacity and increase the useful life of photoexcited electrons, thus enhancing the photovoltaic performance of solar cells. Besides, Iqbal et al. (2021) reported that light absorption is related to crystal size. A shift of the optical absorption edge towards higher wavelengths occurred when using nanostructures with a particle size of 11.23 nm instead of nanostructures with a particle size of 4.12 nm. In comparison with TiO_2 nanostructures, the TiO_2/ZnO hybrid nanostructures presented lower intensity in photoluminescence spectra, indicating a higher photocatalytic activity and a lower recombination rate of photogenerated electron-hole pairs.

In addition, TiO_2/ZnO hybrid nanostructures have also shown excellent results in the field of photodegradation of pollutants in water. According to different publications (Bai et al., 2021; Gupta et al., 2020; Q. Jiang et al., 2022; Xiong Zhang, Guanghui Chen, 2019), it is possible to generate highly active groups with strong oxidizing properties ($^{\bullet}OH^-$ and $\cdot O_2^-$) to degrade water pollutants. The use of TiO_2/ZnO hybrid nanostructures as photocatalysts leads to a rapid separation of charges, which increases the transfer of electrons and holes with the reaction medium. This is because photogenerated electrons from the conduction band of ZnO can move to the conduction band of TiO_2, while photogenerated holes from the valence band of TiO_2 can move to the valence band of ZnO, which decreases recombination processes.

On the other hand, the formation of TiO_2/ZnO hybrid nanostructures may involve the formation of Ti-O-Zn structures. The formation of this type of heterojunctions is evidenced by X-Ray Photoelectron Spectroscopy (XPS) and X-Ray Diffraction (XRD) (Bai et al., 2018; Iqbal et al., 2021; Q. Jiang et al., 2022; X. Jiang et al., 2022). In an investigation carried out by X. Jiang (2022) a different interfacial structure was observed for TiO_2/ZnO nanostructures, in which both semiconductors were in close contact. The absorption edge of the TiO_2/ZnO heterojunction composite was slightly red-shifted compared to pure TiO_2 and ZnO. Furthermore, TiO_2/ZnO hybrid composites presented a lower band gap than pure TiO_2 and ZnO due to the intercalation of their valence and conduction bands. It could be attributed to a greater number of defects produced by ZnO doping within the TiO_2 network, which allowed to trap efficiently photogenerated electrons and promote charge transfer processes. The XPS results showed that the photoelectron peaks of Ti 2p shifted towards higher binding energies, while the photoelectron peaks of Zn 2p shifted towards lower binding energies. These results demonstrated the formation of Ti-O-Zn bonds in the heterojunction composite and an

accumulation of negative charge around the Zn atom, indicating the existence of strong electronic coupling interfaces in the heterojunction composite.

3.2. Methods to synthesise TiO_2/ZnO hybrid nanostructures

In literature, there are many processes to synthesise TiO_2/ZnO hybrid nanostructures such as the hydrothermal method, ultrasonic precipitation, sol-gel, pulsed DC reactive magnetron sputtering, atomic layer deposition, spray pyrolysis, electrodeposition process, or the thermal decomposition, among others. However, in most of the research, hydrothermal, sol-gel and electrodeposition methods are used.

A description of the hydrothermal method, the sol-gel method and the electrodeposition process will be made in the following section. In particular, the ZnO electrodeposition on TiO_2 will be deeply analysed. Furthermore, the electrodeposition conditions reported in literature and their influence on the synthesis of TiO_2/ZnO hybrid nanostructures will be examined.

3.2.1. Hydrothermal method

In a general way, the hydrothermal method is defined as any heterogeneous or homogeneous reaction carried out in presence of solvents or minerals dissolved in aqueous conditions in a closed system under pressures above 1 atm and temperatures above 100 °C (Byrappa and Yoshimura, 2013). It is common to use high temperatures and pressures to dissolve and crystallise materials that are difficult to dissolve under ambient conditions. In addition, the hydrothermal method usually requires long reaction times. This method is environmentally friendly because the reaction takes place in a closed system and the reagents can be recovered and reused. The morphology and the phase composition obtained depend on the temperature, pressure, concentration of

chemical species, duration of the process and pH (Polsongkram et al., 2008; Siwińska-Stefańska et al., 2019; Xu et al., 2011). Furthermore, hydrothermal treatments have been reported to significantly influence the degree of crystallization of TiO_2/ZnO composites, compared to non-hydrothermally treated samples. Both the increase in temperature and the treatment time improve the crystallinity of the synthesised samples (Xu et al., 2011). Moreover, it has also been reported that depending on the ratio of TiO_2 and ZnO under certain hydrothermal synthesis conditions, a higher or lower degree of crystallinity can be obtained (Aal et al., 2008).

With this technique, it is possible to add ZnO on TiO_2 nanostructures both in nanostructured shape and nanoparticles. In this context, Liu et al. (2014) synthesised TiO_2 nanotubes with ZnO nanoparticles for antibacterial applications. First, TiO_2 nanotubes were synthesised by anodization of Ti in an electrolyte composed of ethylene glycol with 0.3 % NH_4F at 30 V for 2 h and annealed at 450 °C for 3 h. After that, ZnO was introduced into TiO_2 nanotubes immersing the samples into an aqueous solution containing different zinc nitrate ($Zn(NO_3)_2$) concentrations (5 - 75 mM) with hexamethylenetetramine ($(CH_2)_6N_4$) at a 1:2 molar ratio and 2 mg of citric acid. The hydrothermal reaction was carried out at 70 °C for 2 h. ZnO particles were homogeneously distributed over the entire surface of TiO_2 nanotubes. The size and amount of ZnO could be controlled by adjusting the concentration of $Zn(NO_3)_2$ and $(CH_2)_6N_4$. The size and amount of ZnO nanoparticles increased as the $Zn(NO_3)_2$ concentration increased. If, instead of nanoparticles, it is intended to form ZnO nanorods, it is enough to use an aqueous solution composed of 20 mM $Zn(NO_3)_2$ and 0.3 - 0.4 M ammonium hydroxide (NH_4OH). The reaction was performed in an autoclave with temperatures between 80 and 160 ° C for 24 h. The hydrothermal process resulted in epitaxial growth of ZnO nanorods oriented through the

inner channels of TiO_2 nanotubes. ZnO nanorods presented an hexagonal wurtzite structure with high crystallinity (Benkara and Zerkout, 2010).

3.2.2. Sol-gel method

The sol-gel process makes it possible to elaborate thin films of a solid material from solutions using a sol or a gel as an intermediate step. The synthesis often involves wet chemistry reactions and sol-gel chemistry to transform molecular precursors into an oxide network. The temperatures used to carry out hydrolysis and condensation reactions are lower than the one used in traditional methods. The process can be simplified into three stages. Firstly, the precursor solution is prepared, secondly, the sol is deposited on the substrate and finally, a heat treatment is performed on the dried gel (xerogel film) (Znaidi, 2010).

With the sol-gel method, TiO_2/ZnO hybrid nanostructures can be obtained from nitrates, inorganic salts and organic salts. The synthesis process of TiO_2/ZnO films consists of two steps. The first one is the formation of alkoxides or alkoxy-complexes. In the second step, these complexes are transformed into oxides through hydrolysis and polymerization reactions. The main parameters that have an influence on the synthesis are the type of solvent, pH, nature and concentration of precursor, duration of the process, additives and the nature of the substrate (Georgakopoulos et al., 2015; Moradi et al., 2016; Naseri et al., 2011; Pérez-González et al., 2015; Znaidi, 2010). For example, TiO_2/ZnO films were prepared via sol-gel using titanium alkoxide and zinc acetate as precursors. On the one hand, a solution of titanium(IV) n-butoxide in ethanol (1:30) was prepared. Subsequently, water was dropped to produce the hydrolysis of the titanium alkoxide and, finally, pH was adjusted to 1.5 by adding nitric acid (HNO_3). On the other hand, a solution of zinc acetate dehydrated in ethylene glycol (1:0.2) was prepared and it was heated for 45 min

for dehydration. Once the precursors were prepared, the deposition of sols on quartz plates was carried out using the dip-coating method. The sols were mixed in Ti / (Ti + Zn) ratios between 25 and 75 % and calcined at 500 °C for 1 h. Results showed a uniform distribution of the two types of nanoparticles whose phases were anatase (TiO_2) and wurtzite (ZnO) (Georgakopoulos et al., 2015). The composition and particle size varied depending on the ratio of the precursor solution (Georgakopoulos et al., 2015; Moradi et al., 2016).

3.2.3. Electrodeposition process

Electrodeposition process is a simple, cost-effective and easy to scale method that enables to synthesise semiconductor nanostructures in the form of thin films deposited on substrates. Film thickness, morphology and growth rate can be easily controlled by modifying deposition potential, time, temperature and the precursor concentration. Physical and chemical properties of the final products depend on the effects of the reaction parameters and mechanisms (Yilmaz and Unal, 2016). The electrodeposition process consists of coating a metallic substrate with a film of a conductive or semiconductor material formed from the electrochemical reduction of metal ions present in an electrolyte. In most cases, the deposit obtained is in crystalline phase, which is an advantage for photoelectrochemical applications. The electrolyte is composed of positive and negative ions from a chemical species containing metallic ions, which will serve as a precursor to the coating material. The process is carried out in an electrochemical cell composed of three electrodes and a potentiostat connected by an electrical circuit. On the one hand, the cathode (metal support on which the electrodeposition will be carried out) is connected to the negative pole of the source. On the other hand, the anode (counter-electrode) is connected to the positive pole of the source. Metal ions will be reduced to

metal atoms, which will form a coating on the cathode surface. In addition, a reference electrode with a well-known and stable electrode potential is also used. The potential of the cathode is measured with respect to the reference electrode in the electrochemical cell. The applied potential depends on the material to be electrodeposited (Ii, 2000; Zangari, 2018).

One of the most used methods to synthesise TiO_2/ZnO hybrid nanostructures is based on the electrodeposition of ZnO on TiO_2 nanostructures. The main advantage of the ZnO electrodeposition process is that it can be carried out at low temperatures, atmospheric pressure and short times (Jiang et al., 2007; Otani et al., 2006; Sánchez-Tovar et al., 2020; Skompska and Zarebska, 2014). ZnO electrodeposition process consists of generating OH^- ions on the TiO_2 surface by effect of the reduction of precursors such as NO_3^-, O_2 and H_2O_2. ZnO electrodeposition was carried out for the first time by Izak and Omi (Izaki and Omi, 1996) using $Zn(NO_3)_2$ as a precursor. The ZnO formation from $Zn(NO_3)_2$ is based on the reduction of nitrates, Zn^{2+} ions behave both as catalysts during the reduction reaction and as reagents during the ZnO precipitation (Yilmaz and Unal, 2016). The following equations (Eqs. 1 to 3) describe the mechanism of ZnO formation from the reduction of $Zn(NO_3)_2$. Eq. 4 describes the entire process.

$$NO_3^- + H_2O + 2\ e^- \rightarrow NO_2^- + 2\ OH^- \quad (1)$$

$$Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2 \quad (2)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (3)$$

$$Zn^{2+} + NO_3^- + 2\ e^- \rightarrow ZnO + NO_2^- \quad (4)$$

The electroreduction of nitrate ions present in the electrolyte (coming from the precursor solution of $Zn(NO_3)_2$) occurs when a negative potential is applied. The reduction reaction is catalysed by Zn^{2+} ions and gives rise to the formation of OH^- ions, which are absorbed on the TiO_2 surface (Eq. 1). As a consequence, the pH of the solution increases in the proximity of the TiO_2. Subsequently, the OH^- ions located on the surface of the TiO_2 react with Zn^{2+} ions producing the precipitation of zinc hydroxide ($Zn(OH)_2$) (Eq. 2). $Zn(OH)_2$ is easily dissolved in aqueous solutions at pH between 9 and 11.2 at 25 °C and between pH 7.8 and 10.5 at 75 °C. Finally, ZnO is formed by the effect of the dehydration reaction of the compound $Zn(OH)_2$ (Eq. 3), and it adheres to the TiO_2 surface to form TiO_2/ZnO hybrid nanostructures. Eq. 4 summarizes the entire process of ZnO formation from $Zn(NO_3)_2$ (Sánchez-Tovar et al., 2020; Skompska and Zarebska, 2014; Yilmaz and Unal, 2016).

ZnO electrodeposition is usually performed with electrolytes composed of zinc nitrate (Otani et al., 2006; Sun et al., 2012; Xue et al., 2011; Yilmaz and Unal, 2016; Yoshida et al., 2004), zinc chloride (Goux et al., 2005; Kumar and Sasikumar, 2014), or zinc acetate (Inamdar et al., 2010, 2008; Karuppuchamy and Ito, 2008). The characteristics of the synthesised ZnO nanostructures can be modified by controlling the temperature, potential, time and precursor concentration. In different research (Chen et al., 2013; Dai et al., 2013; Elias and Le, 2008; Jiang et al., 2007; Lin et al., 2011; Marotti et al., 2006; Otani et al., 2006; Pradhan and Leung, 2008; Prasad et al., 2012; Skompska and Zarebska, 2014) it has been reported that these parameters affect significantly the morphology and orientation of nanostructures, the degree of crystallinity, the particle size, the percentage of defects and the amount of electrodeposited ZnO. Table 2 shows some examples of the main parameters used to electrodeposit ZnO on TiO_2 nanostructures, according to the research carried out in the last years.

The most widely studied electrolyte to carry out the electrodeposition of ZnO is zinc nitrate. The reaction mechanism has been extensively studied to optimize the physical and chemical properties of the final products. Parameters such as $Zn(NO_3)_2$ concentration, temperature and potential have been studied.

3.2.3.1. Influence of $Zn(NO_3)_2$ concentration

The effect of precursor concentration on the morphology and photoelectrochemical properties of nanostructures formed by ZnO electrodeposition has been widely reported. Zn^{2+} ions behave as catalysts for nitrate reduction reaction and as reagents during the precipitation of ZnO (Yilmaz and Unal, 2016). The morphology of nanostructures formed by ZnO electrodeposition can be modified by controlling the concentration of precursors. Different structures have been obtained such as nanowires (Elias and Le, 2008; Prasad et al., 2012), nanorods (Frade et al., 2016; Lin et al., 2011), nanopillars (Elias and Le, 2008), nanowalls (Liang et al., 2013; Pradhan et al., 2010), nanospikes (Pradhan and Leung, 2008) and nanosheets (Ng et al., 2015; Xue et al., 2011). In the case of the deposition of ZnO nanoparticles, both the size and the number of crystals increase with the $Zn(NO_3)_2$ concentration. The electrodeposition method allows us to deposit hexagonal wurtzite ZnO on the surface of a substrate homogeneously. Additionally, the roughness of TiO/ZnO hybrid nanostructures increases with the amount of electrodeposited ZnO (Sánchez-Tovar et al., 2020).

At high concentrations of Zn^{2+}, OH^- ions from the reduction of NO_3^- (Eq. 2) react immediately producing the precipitation of ZnO. ZnO electrodeposition is limited by the rate constant of NO_3^- reduction ($5.98.10^{-10}$ $cm^2 \cdot s^{-1}$) (Yoshida et al., 2004). On the one hand, if the diffusion of Zn^{2+} is significantly lower than the formation rate of OH^-, the ZnO will grow longitudinally. On the other hand, if the diffusion of Zn^{2+} is of the same

order as the formation rate of OH^-, the ZnO will grow both longitudinally and transversely. Since the diffusion of Zn^{2+} ions depends on the concentration gradient, the transverse or longitudinal growth of the ZnO nanostructures can be controlled with the concentration of $Zn(NO_3)_2$ (Skompska and Zarebska, 2014). For example, in order to obtain well-separated and defined nanorods, it is necessary to use $Zn(NO_3)_2$ concentrations lower than 5.10^{-3} M, or increase the concentration of OH^- ions using salts such as $NaNO_3$ and/or increase the potential to accelerate the charge transfer at the electrode/electrolyte interface (Lin et al., 2011; Xue et al., 2011). Sun et al. (2012) demonstrated that modifying the concentration of Zn^{2+} and OH^- ions produces great changes in the aspect ratio, quality and arrangement of the electrodeposited nanorods. Figure 7 shows the relationship between the $Zn(NO_3)_2$ concentration and the diameter and coverage ratio (%) of ZnO nanorods electrodeposited at –1.1 V vs Ag/AgCl (3 M KCl) at 80 °C for 30 min.

In order to obtain a more precise control of the growth process, more complex systems are required. Different studies have been carried out to improve the performance of ZnO nanostructures by modifying their morphology adding organic or inorganic compounds to the electrolyte (Chen et al., 2013; Xu et al., 2009, 2007; Yilmaz and Unal, 2016). For instance, the effect of $Zn(NO_3)_2$ concentration has been studied when adding different amounts of KCl (0 - 1 M). KCl is a capping reagent that hinders the growth of the (001) planes of ZnO. This phenomenon could be caused by the absorption of Cl^- ions. Furthermore, the addition of 1 M KCl produces the electrodeposition of Zn as a consequence of two effects: improving the electrical conductivity of the electrolyte and increasing the electrochemical transfer of Zn^{2+} at the cathode. First, the addition of KCl improves the electrical conductivity of the electrolyte, which results in an increase in the electrodeposition overpotential of the electrolyte. Second, KCl increases the

electrochemical transfer of Zn^{2+} at the cathode, which results in a decrease in the overpotential required to reduce Zn^{2+} ions to Zn. However, the addition of Cl^{-} ions could cause the formation of the zinc chloride hydroxide monohydrate $Zn_5(OH)_8Cl_2 \cdot H_2O$, thus reducing the crystallinity of electrodeposited ZnO. The results also determined that it is possible to modify the morphology of ZnO nanostructures by varying both the KCl concentration and the $Zn(NO_3)_2$ concentration. In electrolytes without KCl, the deposition of ZnO particles took place. However, when the concentration of KCl increased to 1 M, a morphology of ZnO nanospheres and nanosheets was formed. The influence of $Zn(NO_3)_2$ concentration was analysed using a 0.1 M KCl concentration. The morphology of the electrodeposited ZnO varied from nanospikes to nanosheets as the concentration of $Zn(NO_3)_2$ increased from 0.005 M to 0.5 M (Chen et al., 2013).

Yilmaz and Unal (2016) have developed a new combined process to control the morphology of the electrodeposited ZnO. The effect of $Zn(NO_3)_2$ concentration on ZnO nanostructures with a nanorod morphology was studied using an electrodeposition process combined with a hydrothermal method. ZnO electrodeposition was performed in a hydrothermal reactor using a 3-electrode configuration. In this research, ZnO nanorods were electrodeposited using an electrolyte composed of $Zn(NO_3)_2$ at 130 °C at a potential of –1.1 V vs Ag/AgCl (KCl saturated) for 30 min. For this purpose, $Zn(NO_3)_2$ concentrations between 1 and 100 mM were used. The best results were obtained with a concentration of 1 mM $Zn(NO_3)_2$. At this concentration, perpendicular to the surface nanorods with a very small diameter (100 - 200 nm) were obtained. It was concluded that the precursor concentration controlled the aspect ratio of the ZnO rods, and the current density increased with the aspect ratio. This synthesis method provided a simple route to develop nanorods with a desired aspect ratio by controlling the $Zn(NO_3)_2$ concentration.

3.2.3.2. Influence of temperature

Increasing the electrolyte temperature implies an increase in the current density during the ZnO electrodeposition process. According to this, temperature plays a very important role in the acceleration of electrochemical reactions. An important aspect is carried out at the beginning of the process, where the current density decreases quickly. This phenomenon is related to the charge and discharge processes at the substrate/electrolyte interface and to the nucleation of ZnO crystals. The formation of ZnO takes place on the substrate where the reaction of OH^- and Zn^{2+} ions occurs, according to Eqs. 2 and 3. Absorption processes improve as temperature increases, which causes the decrease of the current density in shorter time intervals. The curves of current density versus time increase to a constant value, which increases with temperature. This phenomenon is related to the amount of ZnO crystals formed during the electrodeposition process (Jiang et al., 2007; Sánchez-Tovar et al., 2020).

One of the main steps of the ZnO electrodeposition is the transformation reaction of $Zn(OH)_2$ into ZnO (Eq. 4). This reaction is reversible and it is strongly influenced by the electrodeposition temperature (Skompska and Zarebska, 2014). The stability of $Zn(OH)_2$ and ZnO compounds is limited by the pH of the solution according to Figure 8 (Yamabi and Imai, 2002).

The solid lines of Figure 8 represent the total concentration of soluble Zn^{2+} species as a function of pH, while the dashed lines indicate the thermodynamic equilibria between solid phases and soluble species (Yamabi and Imai, 2002). With solutions at 25 °C, ZnO is formed with concentrations of Zn^{2+} higher than $10^{-5.9}$ mol/dm^3. Both the Zn^{2+} concentration and the pH determine the thermodynamic stability of ZnO (Skompska and Zarebska, 2014). Increasing the temperature produces a change in the solubility curves of

ZnO and $Zn(OH)_2$ towards lower pH values (Goux et al., 2005). For example, $Zn(OH)_2$ is the main soluble specie in the pH range of 9 to 11.2 at 25 °C, while the pH is between 7.8 and 10.5 at 75 °C (Skompska and Zarebska, 2014). The zero net surface charge of ZnO varies according to the pH as a result of two effects: the adsorption of metal hydroxides formed as products of hydrolysis reactions and/or the dissociation of M-OH groups (Degen and Kosec, 2000; Skompska and Zarebska, 2014). The increase in the electrodeposition temperature leads to an increase in the crystallinity of the ZnO film and the preferential orientation in the (002) plane. The size of the crystallites increases as the electrodeposition temperature increases. Furthermore, a shift towards the red absorption edge occurs when increasing the temperature. This displacement is due to an inverse relation with the crystallite size, an effect related to the quantum effects in very small nanoparticles (Marotti et al., 2006; Otani et al., 2006).

In a thermochemical study, ZnO electrodeposition was carried out using a solution of 5 mM $ZnCl_2$ and 0.1 M KCl at temperatures between 25 and 90 °C. It was determined that below 34 °C, the formation of a thin layer of zinc hydroxide occurs, which passivates the surface and hinders the growth of ZnO. However, at temperatures above 34 °C, a continuous growth of ZnO film was observed, obtaining optimum crystallinity and transparency at temperatures above 40 °C. This phenomenon is due to the fact that the formation of zinc hydroxide is kinetically favoured at low temperature (Goux et al., 2005). Other research demonstrated that at elevated temperatures (above 65 °C), ZnO is deposited directly on the substrate, while at low temperatures (below 60 °C), the nucleation and growth of ZnO occurs at the interface between the ZnO precursor and the substrate (Otani et al., 2006). Size, shape and amount of ZnO crystals vary with the temperature. Increasing the electrodeposition temperature increases both the size and the amount of ZnO crystals (Chen et al., 2013; Sánchez-Tovar et al., 2020). With a confocal

Raman microscopy and X-Ray Diffraction it could be seen that the electrodeposited ZnO was in the hexagonal wurtzite crystalline phase (Chen et al., 2013; Jiang et al., 2007; Otani et al., 2006; Sánchez-Tovar et al., 2020).

3.2.3.3. Influence of potential

ZnO electrodeposition process is very sensitive to the potential. The ratio of OH^- ions formation from nitrate reduction is influenced by the applied potential. The amount of OH^- ions increases as the potential increases, which results in a transverse enlargement of the ZnO nanostructures formed. In the case of ZnO nanorods, the higher the applied potential is, the greater the diameter of the ZnO rods will be (Skompska and Zarebska, 2014). ZnO electrodeposition takes place at potentials between –0.8 and 1.2 V, using a reference electrode of Ag/AgCl 3M KCl. In this range of potentials, the growth of the hexagonal ZnO wurtzite takes place mainly in the (002) plane. The optimum potential is approximately –0.9 V vs Ag/AgCl. If the electrodeposition conditions are adjusted to thermodynamic equilibrium, the formation of ZnO nanostructures oriented in the (002) plane is favoured. At negative excessively potentials, the reaction occurs in a non-equilibrium state in which the growth of ZnO takes place rapidly and without predetermined orientation. On the one hand, for potentials greater than –0.8 V vs Ag/AgCl, a very thin ZnO layer is formed. The reduction of nitrate ions is not carried out efficiently as a consequence of the low current density. On the other hand, for potentials lower than –1.3 V vs Ag/AgCl, the cathodic current is triggered, resulting in the electrodeposition of metallic Zn (Jiang et al., 2007).

Marimuthu and Anandhan (2017) synthesised and characterised ZnO nanostructures electrodeposited on TiO_2/ZnO films. TiO_2/ZnO films were synthesised using the spin coating technique followed by annealing to eliminate the organic part and improve the

crystallinity of the samples. Once the TiO_2/ZnO films were synthesised, a ZnO layer was electrodeposited. For this purpose, a solution composed of 0.1 M of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.1 M KCl was used. The function of KCl was to increase the current density and, therefore, it promoted the reduction of nitrates to form OH^- ions that caused the ZnO precipitation. The electrodeposition process was carried out at 70 °C for 10 min with a potential between –1.1 V and –1.3 V vs Ag/AgCl. The results showed that, by increasing the electrodeposition potential, the amount of electrodeposited ZnO also increased. Furthermore, metallic Zn deposition was observed for a potential of –1.3 V vs Ag/AgCl. The Field Emission Scanning Electron Microscopy (FESEM) images showed that the morphology of the nanostructures changed when increasing potential. The nucleation of ZnO crystals increased as potential increased. For a potential of –1.3 V vs Ag/AgCl, the formation of a nanosponge-shaped structure composed of several flowers which had a few nanorods with different orientations took place. According to the results, it was concluded that the photoelectrochemical activity of TiO_2/ZnO hybrid nanostructures can be increased by avoiding the deposition of metallic zinc.

4. Applications of TiO_2/ZnO hybrid nanostructures

4.1. Dye-sensitised solar cell (DSSC)

DSSC is a photoelectrochemical system composed of a dye-sensitised semiconductor oxide film (working electrode) and a platinum counter electrode placed parallel to the working electrode. A liquid or solid electrolyte is introduced between both electrodes, which acts as a conduction media between both electrodes. The light irradiates on the working electrode (photoanode) and photons are absorbed by dye molecules absorbed on the metal oxide. The photons absorbed by dye molecules cause the excitation of the

electrons from the valence band to the conduction band. Subsequently, photoexcited electrons are transferred to the metal oxide where they are transported to the counter electrode through an external electrical circuit. The system is based on a circle process where the electrolyte reduces the oxidised dye molecules, and the electrolyte is regenerated by the electrons injected through the counter electrode. The dye molecules act as an 'antenna' during the photon absorption process (Zhang and Cao, 2011).

DSSC technology faces great challenges due to its poor performance and stability. One of the main components that determines the performance of the devices is the photoanode. Photoanodes are composed of semiconductor metal oxides that act as the backbone of DSSCs. The photoanode is responsible for transporting the photoexcited electrons through the external circuit, which requires a large specific surface area and an effective electron collection (Boro et al., 2018a). TiO_2/ZnO hybrid nanostructures show higher conversion efficiency than TiO_2 nanostructures due to: 1) the increase in dye-loading as a consequence of the increase of the surface area, 2) the decrease in charge recombination due to the interleaving of the valence and conduction bands of TiO_2 and ZnO and 3) the greater separation of charges as a consequence of the biased energy band structure. These factors favour a higher current density during photoelectrochemical tests and, therefore, they improve the conversion efficiency of DSSCs (Boro et al., 2018a; Himmah et al., 2021; Lee et al., 2013; Li et al., 2015; Mane et al., 2005; Marimuthu and Anandhan, 2017; Song et al., 2014).

In a research developed by Xie et al. (2011), coaxial TiO_2/ZnO nanotubes arrays were formed by electrochemical methods to use them as photoanodes. FESEM images showed that ZnO was homogeneously deposited in the inner of the tubes, without covering the pores of TiO_2 nanotubes. The electrodeposited ZnO increased the roughness of the inner

surface of the tubes, which favoured the dye loading and the electrolyte transport. A general energy conversion efficiency of 2.8% was obtained, which was 40 % higher than the one obtained with pure TiO_2 nanotubes. The improvement was caused due to the fact that the ZnO layer increased the specific surface area and the amount of adsorbed dye, improved the charge separation at TiO_2/ZnO interface and decreased the recombination processes. Figure 9a shows the comparison between the I-V curves obtained in DSCCs systems using TiO_2 nanotubes and coaxial TiO_2/ZnO nanotubes. In addition, incident photon-to-electron conversion efficiency (IPCE) spectra are also shown (Figure 9b).

Lee et al. (2013) also successfully fabricated TiO_2/ZnO hybrid nanostructures by anodization of TiO_2 nanotubes followed by ZnO electrodeposition. They observed that the size of the electrodeposited ZnO nanoparticles increased as the electrodeposition time increased. ZnO was electrodeposited both on the outer and inner surfaces of TiO_2 nanotubes, which resulted in an increase in the specific surface area. The performance of DSSCs is significantly affected by the amount of dye absorbed at the photoanode. DSSCs formed by TiO_2 nanotubes with ZnO electrodeposited for 50 s showed the highest efficiency (3.18 %) due to the fact that they showed the highest current density during the photoelectrochemical tests (Lee et al., 2013). In another research carried out by Li et al. (2015), porous TiO_2/ZnO nanodonuts were synthesised by electrospray process varying the ZnO concentrations. The highest performance was obtained for the sample with a ZnO molar ratio of 4 %. It showed the highest dye absorption, the best light scattering and the highest electron transport. With this nanostructure, an energy conversion efficiency of 9 % was obtained. Although the use of TiO_2/ZnO hybrid nanostructures for solar cells is on the up, since 2009 perovskite cells have made rapid progress, obtaining a performance over 19 % (Boro et al., 2018b).

4.2. Decontamination

Photocatalytic degradation of organic pollutants in wastewaters is a low cost and environmentally friendly method. This process is based on the generation of hydroxyl-free radicals (Eq. 5) due to the effect of the holes (h^+) generated in the valence band (VB) of a semiconductor material (photocatalyst) when irradiated with light of a certain wavelength. These hydroxyl-free radicals ($^{\bullet}OH$) are capable of degrading the pollutants adsorbed on the surface of the photocatalyst (S) into harmless products (Velempini et al., 2021). In addition, the photoexcited electrons of the conduction band (CB) trapped oxygen molecules to form super oxygen radicals (Eq. 6), which degrade the absorbed contaminant on photocatalyst surface or react to form $^{\bullet}OH$ (Eqs. 7, 8, 9).

$$S(h^+_{VB}) + H_2O \rightarrow S + H^+ + {}^{\bullet}OH \quad \text{Eq. 5}$$

$$e^-_{CB} + O_2 \rightarrow {}^{\bullet}O_2^- \quad \text{Eq. 6}$$

$$^{\bullet}O_2^- + H^+ \rightarrow {}^{\bullet}HO_2 \quad \text{Eq. 7}$$

$$2\ {}^{\bullet}HO_2 \rightarrow H_2O_2 \quad \text{Eq. 8}$$

$$H_2O_2 \rightarrow 2{}^{\bullet}OH \quad \text{Eq. 9}$$

In recent years, the use of TiO_2/ZnO hybrid photocatalysts for degradation applications of contaminants in water has gained interest due to their ability to intercalate their valence and conduction bands, reducing the recombination processes of electron-hole pairs (Abdel-wahed et al., 2021; Fatimah and Novitasari, 2016; Hashem and Abdal-hay, 2021; Lee et al., 2019; Liu et al., 2017; Siwińska-Stefańska et al., 2018; Tobajas et al., 2017; Velempini et al., 2021). Lee et al. (2019) synthesised one-dimensional TiO_2/ZnO nanofibers of different diameters using an electrospinning process. The photoelectrochemical characterization of these nanofibers was carried out from the results obtained from photoelectrochemical degradation of methylene blue using UV irradiation.

Methylene blue decomposition was carried out without nanofibers, with TiO_2 nanofibers and with TiO_2/ZnO nanofibers. The results indicated a degradation rate of 12.6 % for the degradation system without nanofibers, 41.9 % with TiO_2 nanofibers and 96.3 % with the TiO_2/ZnO nanofibers with the optimal diameter (400 nm). Nanofibers with a small diameter have a large specific surface area, so they present excellent photocatalytic and bio-friendly properties.

Fatimah and Novitasari (2016) used TiO_2/ZnO hybrid nanostructures to degrade phenol using a new method that combined the method of degradation by sonication and photocatalysis. TiO_2/ZnO hybrid nanostructures were synthesised by the sol-gel method in a mole ratio Ti:Zn = 5:1. TiO_2/ZnO hybrid nanostructures showed higher surface area and pore volume compared to TiO_2 and ZnO nanostructures. The sonophotocatalysis results obtained with hybrid nanostructures showed a 99.31 % degradation after 1 hour. In another research, TiO_2/ZnO hybrid nanostructures were fabricated using a sol-gel method with different Ti:Zn mole ratios (9:1, 5:2 and 1:3). The photocatalytic activity of the samples was evaluated by photochemical decomposition under UV irradiation using the following organic dyes: Basic Blue, Basic Red and Basic Violet. The kinetic analysis of the results showed that the dyes degradation was more intense in nanostructures synthesised with a TiO_2:ZnO ratio of 9:1. These nanostructures showed the highest photocatalytic activity and they degraded between the 93 and 98 % of the studied dyes (Siwińska-Stefańska et al., 2018).

The photocatalytic activity of TiO_2/ZnO hybrid nanostructures has also been evaluated through the degradation of P-Cresol. Brooms et al. (2017) synthesised TiO_2/ZnO hybrid nanostructures by the precipitation of ZnO on the surface of commercial TiO_2 (Degussa P-25, Aeroxide). In addition, they formed a new photocatalyst based on TiO_2/ZnO hybrid

nanostructures modified with polyaniline (PANI) to improve the performance of the nanostructures. The formation of TiO_2/ZnO heterojunctions improved quantum efficiency and decreased the recombination rate of electron-hole pairs, showing better results in P-Cresol degradation than commercial TiO_2 nanoparticles and ZnO nanoparticles formed by precipitation (Figure 10).

Recently, Liu et al. (2017) also revealed the promising applications for the decontamination of persistent organic pollutants in water that TiO_2/ZnO hybrid nanostructures are offering. They synthesised a new type of TiO_2/ZnO hybrid nanostructure based on hollow microspheres. The hollow structure significantly increased the surface area and the optical properties. The synthesis was carried out with a one-step hydrothermal method using different reaction times (6, 12, 18 and 24 h). In addition, TiO_2 and ZnO nanostructures were synthesised using the same procedure. Photocatalytic activity was evaluated by degradation of 2,4-Dinitrophenol (2,4-DNP) under simulated sunlight irradiation. The photocatalytic activity of the TiO_2/ZnO hybrid nanostructures that showed the best degradation rate was compared with the results obtained from TiO_2 and ZnO nanostructures (Figure 11a). TiO_2/ZnO hybrid nanostructures synthesised with a reaction time of 24 h exhibited a higher apparent reaction rate constant (0.167 min^{-1}) than that obtained from TiO_2 (0.107 min^{-1}) and ZnO (0.07 min^{-1}). Furthermore, the removal TOC was much higher for TiO_2/ZnO hybrid nanostructures (78 %) compared to that obtained with TiO_2 (53 %) and ZnO (45 %). Therefore, most of the organic carbon present in the water was degraded into final products, which was very beneficial for water decontamination applications. Moreover, the samples were also compared with Commercial P25 (TiO_2 nanoparticles). TiO/ZnO hollow microspheres were able to degrade 10 mg/L in 20 min, while the P25 needed approximately 25 min (Figure 11b).

In a research carried out by Wang et al. (2013), a sample of the wastewater from a pharmaceutical factory was taken to photocatalytically decompose organic and inorganic pollutants present in it. Photocatalytic degradations were carried out under ultraviolet irradiation for 2 hours using TiO_2/ZnO composites as photocatalysts. The degradation of pharmaceutical wastewater pollutants was evaluated by decolouration and chemical oxygen demands (COD) removal tests. The decolouration and COD removal rates of the pharmaceutical wastewater were 45.8 % and 79.0 %, respectively, when the optimal TiO_2/ZnO composites were used as photocatalysts.

4.3. Photoelectrochemical water splitting

Photoelectrochemical water splitting has attracted the attention of the scientific community in recent years. This is a method to produce hydrogen (H_2) that combines the electrolysis of water and photocatalysis in a single element. When the electrical energy necessary to carry out the process is obtained from renewable energy sources, it is considered a totally sustainable method, due to the abundance of the necessary resources (water and sunlight), and an environmentally friendly method with zero carbon emissions (Acar et al., 2016). During the photoelectrochemical water splitting process, photon energy is converted into chemical energy (H_2). The oxidation and reduction reactions of water take place when a photon is absorbed by the surface of a semiconductor material (photoelectrocatalyst). At that moment, the electrons of the valence band (VB) of the semiconductor move to the conduction band (CB) generating electron-hole pairs. The photoexcited electrons carry out the reduction reaction (H_2 formation) and the holes carry out the oxidation reaction (O_2 formation), see Figure 12. In order to carry out this process, the position of VB and CB is crucial and it must be similar to the oxidation and reduction potential of water, respectively (Kochuveedu, 2016).

One of the main limitations of this method is the recombination processes. When electron-hole pairs are not efficiently separated, electrons and holes instantly recombine without carrying out oxidation and reduction reactions. For this reason, charge separation is a crucial factor in the photocatalytic activity of the semiconductors. In this context, TiO_2/ZnO hybrid nanostructures are being widely studied because apart from presenting a high photocatalytic activity, their valence and conduction bands are interspersed when both semiconductors are combined, which allows the movement of electrons and holes, reducing recombination processes (see Figure 13) (Feng et al., 2017).

Recently, promising TiO_2/ZnO nanorods have been designed to be used as photoanodes in efficient photoelectrochemical cells. The results showed that performing an appropriate ZnO coating on the TiO_2 nanostructures provides a high contact area with the electrolyte, greater light scattering and absorption and an increase in the transfer of photogenerated charge carriers. All these contributions rise the photocurrent response (Feng et al., 2017). Shaheen et al. (2013) fabricated TiO_2/ZnO nanotubes in order to be used as photoelectrodes in photoelectrochemical water splitting processes. TiO_2 nanotubes were synthesised by anodization processes and, subsequently, TiO_2 nanotubes were coated with a layer of ZnO by radio frequency sputtering. Morphology, crystallinity and optical properties of the photoelectrodes depended on the thickness of the ZnO layer. The light absorption of the photoelectrode increased as the thickness of the ZnO layer increased. Optimal TiO_2/ZnO hybrid nanostructures showed an almost 80 % increase in the photoconversion efficiency (7.3 %) compared to pure TiO_2 nanotubes (4.1 %). The improved photocatalytic activity of TiO_2/ZnO nanotubes is related to an increase in the charge carriers collection efficiency, a greater separation of charges and an increase in the surface area. Figure 14 shows the photoelectrochemical results obtained using pure

TiO_2 nanotubes and TiO_2/ZnO nanotubes sputtered for 18, 35 and 53 min as photoelectrodes.

Another example of electrochemical fabrication of TiO_2/ZnO hybrid nanotubes to carry out photoelectrochemical water splitting applications was performed by Mohsen and Yousef (Mohsen and Yousef, 2015). The research consisted of synthesising TiO_2/ZnO nanotubes combining the methods of electrochemical anodization of Ti and chemical bath deposition of ZnO. Once the nanostructures had been synthesised, they were used as photoanodes in a photoelectrochemical cell for hydrogen production. Again, it was observed that by increasing the ZnO amount, the visible light absorption range improved in comparison with pure TiO_2 nanotubes. Furthermore, in this research a progressive decrease in the band-gap energy was observed as the ZnO amount in the nanostructure increased. The results showed that the optimal weight loading of ZnO was 3 %. With these nanostructures it was possible to significantly increase the photocurrent efficiency compared to TiO_2 nanotubes.

Al-Johani et al. (2015) compared the photocatalytic performance of TiO_2/ZnO hybrid nanostructures synthesised by a sol-gel method with commercial TiO_2 nanoparticles (P25). For this purpose, they synthesised TiO_2/ZnO hybrid nanostructures with different concentrations of ZnO (1, 5, 10, 12 and 30 %) and they performed photocatalytic hydrogen production tests under UV irradiation in a solution composed of ethanol/water (50:50). The results showed that moderate concentrations of ZnO considerably improve the performance of the photocatalysts, obtaining the best results for the TiO_2/ZnO hybrid nanostructures formed with 10 % ZnO. These nanostructures showed a photocatalytic hydrogen production of 1047 μmol/h, approximately 43 % higher than that obtained with commercial TiO_2 nanoparticles (595 μmol/h).

4.4. Gas sensors

Metal oxide semiconductors are the most common materials for gas detection due to their high sensitivity and low cost. Metal oxide sensors use redox reactions between the target gases and the oxide surface. The process is based on the reaction between oxygen ions distributed on the oxide surface and the molecules of the target gases. As a result, there is an electronic variation on the oxide surface. This variation produces a change in electrical resistance that can be detected by the change in capacitance that the material undergoes. Therefore, the chemical reaction between the gas and the semiconductor surface and the equivalent changes in the electrical resistance of the sensor are the two most important factors to consider when obtaining highly sensitive sensors. Furthermore, the process is strongly influenced by the operating temperature (Liu et al., 2012).

Tin dioxide (SnO_2) is the most widely used material for gas detection. This is an n-type semiconductor whose electrical conductivity depends on the concentration of oxygen ions absorbed on its surface. Another semiconductor that is used as a sensor is TiO_2. TiO_2 offers high sensitivity in terms of dielectric permittivity to gas adsorption. Transition metal oxides have the advantage of being able to form several oxidation states, compared to non-transition metal oxides that have only one oxidation state (Liu et al., 2012; Malallah Rzaij and Mohsen Abass, 2020). The formation of nanostructured materials and the formation of hybrid compounds with other semiconductor oxides are two optimal solutions to improve the gas detection and the photocatalytic activity of a semiconductor oxide.

In this way, the use of TiO_2/ZnO hybrid nanostructures for gas detection has been studied. For this purpose, nanofibers have attracted great interest because they provide a very high surface/volume ratio and good physical properties. Hashemi et al. (2020) successfully

formed ZnO nanowires on TiO_2/ZnO nanofibers using a combined electrospinning method and hydrothermal process. The nanowires showed a length of 950 nm and a diameter of 70 - 120 nm. UV light absorption was improved due to its highly porous structure and heterojunction regions. The nanostructures showed great sensitivity for 10 - 200 ppm of ethanol gas and a reduced response and recovery times, when using an optimal temperature of 240 - 260 ^oC. The sensitivity of the samples increased about 3 times when using UV light. TiO_2/ZnO nanofibers can also be synthesised by electrospinning of TiO_2 and ZnO deposition by atomic layer deposition. The results showed that the resistance of the sensor increased as the oxygen rate increased and decreased when it was removed. Both sensitivity and dynamic repeatability were found to be appropriate for fabricating sensitive and reliable chemical sensors (Park et al., 2009). In another research, TiO_2/ZnO nanofibers were also formed following a combined method by electrospinning of TiO_2 and ZnO deposition by ALD. The gas sensing was evaluated by detecting 100 ppm NH_3 at 150 and 220 ℃. In this research, the thickness influence of the ZnO layer on the response time was observed. The ZnO deposition by ALD considerably influenced the specific surface area of nanostructures and therefore, their photocatalytic properties. It was concluded that the ZnO deposition films should be as thin as possible in order not to reduce the specific surface area of the nanofibers and thus not to reduce their active surface (Boyadjiev et al., 2017).

Gas sensing performance can be evaluated by the spectral response of a gas detector under different concentrations of the studied gas. Figure 15a shows the wavelength as a function of hydrogen sulfide (H_2S) concentration using a hydrogen sulfide gas sensor based on TiO_2/ZnO composite sensing membrane-coated no-core fiber. Gas detection was monitored in the interference spectrum at 1554 nm in the H_2S concentration range between 0 and 50 ppm. The linear fitting of the results determined that the sensitivity was

21.26 ppm·ppm^{-1}. In addition, the dynamic response of the sensor was also measured (Figure 15b), resulting in a response time of about 90 s and a recovery time of about 115 s (Feng et al., 2021).

4.5. Lithium-ion batteries

Nowadays, lithium-ion battery systems are receiving more and more attention because they offer excellent properties such as high energy density, long life cycle, facility of manufacture and reasonable production costs. Lithium-ion batteries are the main primary power source for portable devices. Its basic operation is based on the ability to convert chemical energy into electric energy through electrochemical oxidation/reduction reactions using a potential difference between the anode and the cathode in the presence of an electrolyte. For this purpose, a solution containing a lithium (Li) salt is used. Li ions are transported between the cathode and the anode while electrons travel through the external circuit providing a current flow. Li ions are intercalated in the cathode during the discharge process, while ions leave the cathode to intercalate in the anode during the charging process. In commercial cells, the anode is composed of carbonaceous materials and the cathode is composed of materials such as lithium transition metal oxides (with a more positive redox potential) (Madian et al., 2018).

Although lithium-ion batteries are attracting great interest, their electrochemical performance still needs improvement. Their efficiency is hampered by some restrictions in the electrode materials. In order to achieve high efficiency, the electrodes should have high surface area and large pore size, low volume expansion/shrinkage during lithium insertion/extraction and high ionic and electrical conductivity. Moreover, the materials are required to be abundant, low cost and non-toxic. For these reasons, the research is aimed to replace the traditional electrodes by new materials. In this context, transition

metal oxides have attracted the interest of researchers. Transition metal oxides have shown high electrochemical capabilities. Among all of them, TiO_2 has been postulated as the most promising. TiO_2 shows high cyclic stability and high efficiency. However, the performance of TiO_2 is limited by its poor electronic conductivity, low ionic diffusivity and insufficient kinetics. The low theoretical capacity of TiO_2 (335 $mA \cdot h \cdot g^{-1}$) hampers the development of high-performance anodes. In addition, its reversible capacity is only 180 $mA \cdot h \cdot g^{-1}$, that is, half of its theoretical capacity (Madian et al., 2018; Nan, 2013). The TiO_2 nanostructuring and the mesoporous structure design can improve its electrochemical behaviour. However, enhancing the performance of batteries by modifying only the morphology of the nanostructures is a great challenge. Therefore, hybridization of TiO_2 with semiconductors such as ZnO could be a better solution (Opra et al., 2019).

TiO_2/ZnO hybrid nanostructures have significant features such as high porosity and mechanical resistance. Kanjwal et al. (2010) prepared TiO_2/ZnO hybrid nanostructures by electrospinning a colloidal solution of titanium isopropoxide/poly(vinyl acetate) zinc nanoparticles. Subsequently, Li^+ ions were intercalated within the nanostructures. They showed a high capacity due to the increase of their surface area to volume ratio, electronic transport and area in the electrode/electrolyte interface. Consequently, reaction kinetics was enhanced and cell capacity, capacity retention and charge/discharge rates increased. The optimal nanostructures exhibited a high-rate capacity (1232 $mA \cdot h \cdot g^{-1}$). In a research performed by Cao et al. (2022), TiO_2/ZnO hybrid nanostructures that allowed the infusion of molten Li^+ into the structure were fabricated. TiO_2/ZnO hybrid nanostructures consisted of TiO_2 nanotube matrices formed by electrochemical anodization and ZnO nanoparticles deposited by thermal hydroxide decomposition. The anode used consisted of a trilayer TiO_2/ZnO/Li structure that showed great stability during the electroplating

and Li metal stripping. TiO_2 nanotube array functioned as a structural support and ZnO particles allowed for the uniform nucleation of Li metal without overpotential. Compared with Li foil anode, the hybrid nanostructure showed improved cyclic stability, high and stable coulombic efficiency and lower hysteresis.

In a research carried out by Zhang et al. (2019), lithium-ion battery cells were formed using TiO_2/ZnO hollow nanoflower arrays as anodes. The charge-discharge voltage profiles at a constant current rate of 200 $mA \cdot g^{-1}$ of the TiO_2/ZnO hollow nanoflower arrays showed an initial charge and discharge capacity of 1240 $mA \cdot h \cdot g^{-1}$ and 1028 $mA \cdot h \cdot g^{-1}$ (Figure 16a), respectively. In addition, the cycling performance of TiO_2/ZnO hollow nanoflower arrays was compared with the cycling performance of pure TiO_2 hollow nanofiber arrays and pure ZnO nanorod arrays (Figure 16b), synthesised by the same method used to form the TiO_2/ZnO hollow nanoflowers arrays. After 200 cycles, TiO_2 hollow nanofiber arrays showed excellent cyclic capacity retention but very low discharge capacity, while ZnO nanorod arrays showed high discharge capacity but very low cyclic capacity retention. However, TiO_2/ZnO hollow nanoflower arrays showed both good discharge capacity and high cyclic capacity retention, obtaining a coulombic efficiency of 98.3 % after 200 cycles. Therefore, TiO_2/ZnO hollow nanoflower arrays inherited the high capacity of pure ZnO nanorod arrays and the excellent rate performance of TiO_2 hollow nanofiber arrays.

4.6. Novel applications

Although the most interesting applications for TiO_2/ZnO hybrid nanostructures are the photocatalytic degradation of pollutants, photoelectrochemical production of hydrogen and solar cells, new applications continue to emerge such as the UV photodetectors,

lasers, light-emitting diodes, adsorption of chemical compounds and antibacterial capacity, among others.

The optical properties (refractive index, absorption coefficient, dielectric constant, photoconductivity, etc.) of a semiconductor material are closely related to its band gap. The high sensitivity/response to UV light of TiO_2/ZnO hybrid nanostructures makes them a very suitable material for the fabrication of UV light photodetectors (AlDabagh et al., 2016; Hsu et al., 2018; Shao et al., 2014; Zhang et al., 2015). UV photodetectors have attracted the attention of researchers due to their potential in applications such as remote control, water purification, chemical analysis, flame detection, etc. (Mazhir et al., 2015). Both the energy level of intrinsic defects of the materials and the level of doping play an essential role in influencing the optical properties and wavelength detection of TiO_2/ZnO hybrid nanostructures. Heterojunctions have been widely used as a basic building block of photoelectric devices. This is due to its unique microstructural, interfacial and electronic characteristics. The electric fields formed at the interfaces allow the efficient separation of the photogenerated electron-hole pairs to regulate the transport of the charge carriers, thus improving the photoelectric properties, such as self-powering and/or rectification characteristics, on-off ratio, spectral response range, etc (Li et al., 2022). AlDabagh et al. (2016) synthesised TiO_2 films doped with ZnO (5 % and 7%) using the pulse laser deposition technique to use them as UV photodetectors. The TiO_2/ZnO-based devices showed higher responsivity, quantum efficiency and specific detectivity than the devices based on TiO_2 films, showing a responsivity of 3.82 A/W with a ZnO doping of 7 %.

Another example of exploiting the optical and optoelectronic properties of TiO_2/ZnO hybrid nanostructures is their use in organic light-emitting diode (OLED) lighting

devices. OLED performance can be improved by inserting light extraction layers to improve the light release capability of the devices. The light extraction methods can be divided into internal and external methods. The external extraction method is based on coating the outside of the device with an optical film layer. This method does not affect the device performance because the working layer is applied on the outside of the device. The improvement in light extraction and electroluminescence spectrum depends on the refractive index and the size and thickness of the optical film layer (Kubiak et al., 2021; Park et al., 2017; Zhou et al., 2020). In an investigation carried out by Park et al. (2017), the use of a light extraction layers composed of TiO_2/ZnO nanoparticles in OLED devices was studied, observing an increase in the luminescence of the devices. Both the luminescence efficiency and the quantum efficiency increased with respect to those obtained without the light extraction layer and those obtained with a TiO_2 nanoparticle extraction layer.

In addition, in recent years, the ability of TiO_2/ZnO hybrid nanostructures to be used as adsorbent materials has also been studied. For this application, one of the most important factors is that the nanostructures used have a high specific surface area with a high pore volume. From the study of the adsorption kinetics of a certain adsorbent, the adsorption process can be modelled and designed and variables such as the residence time or the maximum sorption capacity of an adsorbent ($mg \cdot g^{-1}$) can be determined (Elfiky and Salahuddin, 2021; Jain et al., 2017; Khosravi et al., 2020; Waghmode et al., 2016). In an investigation carried out by Khosravi, TiO_2/ZnO nanofibers were synthesised on sewage sludge carbon (SSC) by electrospinning to adsorb Ni(II), Cu(II) and chemical oxygen demands (COD) from aqueous solutions and industrial wastewaters of Iran. The formed SSC/TiO_2/ZnO nanofibers showed a high specific surface area (685.6 $m^2 \cdot g^{-1}$), compared to the sewage sludge carbon support (18 $m^2 \cdot g^{-1}$). The kinetic parameters of the

SSC/TiO2/ZnO nanofibers showed a pseudo-second-order kinetics model under the optimal conditions. The chemical adsorption was the rate controlling step and the adsorption sites were proportional to the square of the number of unoccupied sites of adsorbent. Influence of pH, adsorbent dosage and contact time were studied to optimise the adsorption process. The maximum monolayer sorption capacities of Ni(II), Cu(II) and COD were 282.3 $m^2 \cdot g^{-1}$, 298.1 $m^2 \cdot g^{-1}$ and 2220.3 $m^2 \cdot g^{-1}$, respectively, for the optimal adsorption parameters. Finally, the results were compared with other adsorbent nanofibers present in the literature (Table 3), showing greater sorption capacity than most of them (Khosravi et al., 2020).

Another characteristic of TiO_2/ZnO hybrid nanostructures is their good antimicrobial and antibacterial activity. The use of Ti in biological applications is widely standardised due to its high chemical stability, while the antimicrobial and antifungal activity of ZnO has also been reported in several investigations (Anaya-Esparza et al., 2019; Aydin et al., 2021; Chabalala et al., 2021; Zhang et al., 2018). In addition, it has been reported that the morphology of nanostructured materials offers active sites for protein adsorption, which increases cell-implant interaction (Tan et al., 2012). These properties are some of the characteristics that have led the scientific community to study the use of TiO_2/ZnO hybrid nanostructures in biological applications. Aydin et al. (2021) studied the antibacterial/antifungal activity of TiO_2 nanotubes formed by electrochemical anodization doped, on the one hand, with Ag nanoparticles and, on the other hand, with ZnO nanorods. In addition, the corrosion behaviour of the nanostructures in simulated body fluid (SBF) solution was also examined. The corrosion results showed that the incorporation of the ZnO nanorods increased the protection against corrosion by interrupting contact of the metal/solution. On the one hand, TiO_2 nanotubes doped with silver (Ag) nanoparticles exhibited high antibacterial activity. The addition of Ag

nanoparticles increased the antibacterial activity as a consequence of the blockage of the enzymatic system of the respiratory chain. This could be related to the formation of superoxide anion radicals, which react with H^+ ions to produce H_2O_2 molecules, which would penetrate the cell membrane, changing the DNA synthesis. On the other hand, TiO_2/ZnO hybrid nanotubes showed a high antifungal activity. The addition of ZnO nanotubes improved the fungal growth inhibition capacity as a consequence of a higher separation of charge carriers, which resulted in a decline in the recombination rate.

5. Conclusion

In this work, the main synthesis methods and applications for TiO_2/ZnO hybrid nanostructures have been presented. It focuses on the formation of TiO_2/ZnO hybrid nanostructures from electrochemical methods to use them as semiconductor materials in different applications. The detailed procedures are based on the addition of ZnO on TiO_2 nanostructures. The key points of this review are summarized below.

Photoelectrocatalysis is a discipline that uses electricity and light radiation as an energy source. The most widely used photoelectrocatalyst is TiO_2 due to its good photochemical properties. However, TiO_2 has several limitations such as a poor charge transport and a rapid recombination of photoexcited charge carriers. In order to overcome these limitations, TiO_2/ZnO hybrid nanostructures can be obtained. The main advantage of TiO_2/ZnO hybrid nanostructures over other TiO_2 hybrid materials is that the photoexcited electrons from the conduction band of ZnO can be transferred to the conduction band of TiO_2 and the holes from the valence band of TiO_2 can be transferred to the valence band of ZnO, which reduces the recombination rate of load carriers. In addition, ZnO has greater oxidization capacity of photogenerated holes, better electrical transport properties

and greater electron mobility. Therefore, the photocatalytic activity of TiO_2 improves when it is combined with ZnO.

There are a lot of electrochemical methods to synthesise TiO_2/ZnO hybrid nanostructures. From all of them, this review has highlighted the electrochemical anodization of Ti and the electrodeposition of ZnO. These methods have been widely studied over the years. They allow you to easily control the physical and chemical properties of the synthesised nanostructures. The formation conditions of nanostructures are key parameters to increase the nanostructures growth rate and/or aspect ratio, and the crystallinity and defect structure of nanostructures can be controlled by thermal annealing. On the one hand, the effect of the anodization conditions on TiO_2 nanostructures has been widely studied. The main parameter that determines the morphology of the nanostructures is the composition of the electrolyte. In addition, anodization temperature, potential, time and hydrodynamic conditions also influence the growth of TiO_2. On the other hand, the growth of ZnO crystals on TiO_2 nanostructures caused by the electrodeposition process can be easily controlled by modifying the deposition potential, time, temperature and precursor concentration.

Finally, a review of the main applications for TiO_2/ZnO hybrid nanostructures has been carried out. It has been concluded that the main parameters that influence the photoelectrochemical activity of nanostructures are the morphology, the aspect ratio, the charge carrier's collection efficiency and the separation of charges.

Acknowledgments

The authors would like to thank the financial support to the Agencia Estatal de Investigación (PID2019-105844RB-I00/MCIN/AEI/10.13039/501100011033) and the

co-finance by the European Social Fund. Pedro José Navarro Gázquez also wants to show his gratitude for the concession of the Grant PEJ2018-003596-A-AR funded by MCIN/AEI/10.13039/501100011033 and by “ESF Investing in your future”.

References

Aal, A., Barakat, M., Mohamed, R., 2008. Electrophoreted Zn–TiO2–ZnO nanocomposite coating films for photocatalytic degradation of 2-chlorophenol. Appl. Surf. Sci. 254, 4577–4583. https://doi.org/10.1016/j.apsusc.2008.01.049

Abdel-wahed, M.S., Gad-allah, T.A., Abdel-karim, A., Margha, F.H., 2021. REMEDIATION TREATMENT UV sensitive ZnO and TiO 2 -ZnO nanocrystalline transparent glass-ceramic materials for photocatalytic decontamination of surface water and textile industry wastewater 1–11. https://doi.org/10.1002/ep.13653

Abellán, M.N., Giménez, J., Esplugas, S., 2009. Photocatalytic degradation of antibiotics: The case of sulfamethoxazole and trimethoprim. Catal. Today 144, 131–136. https://doi.org/10.1016/j.cattod.2009.01.051

Acar, C., Dincer, I., Naterer, G.F., 2016. Review of photocatalytic water-splitting methods for sustainable hydrogen production 1449–1473. https://doi.org/10.1002/er

Adams, D.M., Brus, L., Chidsey, C.E.D., Creager, S., Creutz, C., Kagan, C.R., Kamat, P. V., Lieberman, M., Lindsay, S., Marcus, R.A., Metzger, R.M., Michel-Beyerle, M.E., Miller, J.R., Newton, M.D., Rolison, D.R., Sankey, O., Schanze, K.S., Yardley, J., Zhu, X., 2003. Charge transfer on the nanoscale: Current status. J. Phys. Chem. B 107, 6668–6697. https://doi.org/10.1021/jp0268462

Al-Johani, M.S., Al-Zaghayer, Y.S., Al-Mayman, S.I., 2015. TiO 2 / ZnO Photocatalytic Activity for Hydrogen Production.

AlDabagh, S.Y., Aadim, K.A., abbas, T. tariq, 2016. Fabrication of TiO2 Doped ZnO UV Detector by Pulse Laser Deposition. Int. J. Eng. Appl. Sci. 3.

Alivisatos, A.P., 1996. Perspectives on the physical chemistry of semiconductor nanocrystals. J. Phys. Chem. 100, 13226–13239. https://doi.org/10.1021/jp9535506

Allam, N., Grimes, C., 2009. Room Temperature One-Step Polyol Synthesis of Anatase TiO2 Nanotube Arrays: Photoelectrochemical Properties. Langmuir 25, 7234–7240. https://doi.org/10.1021/la9012747

Allen, N.S., Mahdjoub, N., Vishnyakov, V., Kelly, P.J., Kriek, R.J., 2018. The effect of crystalline phase (anatase, brookite and rutile) and size on the photocatalytic activity of calcined polymorphic titanium dioxide (TiO2). Polym. Degrad. Stab. 150, 31–36. https://doi.org/10.1016/j.polymdegradstab.2018.02.008

Anaya-Esparza, L.M., Montalvo-González, E., González-Silva, N., Méndez-Robles, M.D., Romero-Toledo, R., Yahia, E.M., Pérez-Larios, A., 2019. Synthesis and Characterization of TiO2-ZnO-MgO Mixed Oxide and Their Antibacterial Activity. Mater. . https://doi.org/10.3390/ma12050698

Archana, T., Vijayakumar, K., Arivanandhan, M., Jayavel, R., 2019. TiO2 nanostructures with controlled morphology for improved electrical properties of photoanodes and quantum dot sensitized solar cell characteristics. Surfaces and Interfaces 17, 100350. https://doi.org/10.1016/j.surfin.2019.100350

Arin, J., Thongtem, S., Thongtem, T., 2013. Single-step synthesis of ZnO/TiO2 nanocomposites by microwave radiation and their photocatalytic activities. Mater.

Lett. 96, 78–81. https://doi.org/10.1016/j.matlet.2013.01.026

Asgari, V., Noormohammadi, M., Ramazani, A., Kashi, M.A., 2017. A facile method to form highly-ordered TiO2 nanotubes at a stable growth rate of 1000 nm min-1 under 60 v using an organic electrolyte for improved photovoltaic properties. J. Phys. D. Appl. Phys. 50. https://doi.org/10.1088/1361-6463/aa812a

Aydin, E.B., Sığircik, G., Takci, H.A.M., 2021. Antimicrobial properties and corrosion behavior of TiO2NTs electrodes modified with Ag and ZnO nanorod in simulated body fluid solution. J. Mol. Struct. 1240, 130569. https://doi.org/https://doi.org/10.1016/j.molstruc.2021.130569

Bai, N., Liu, X., Li, Z., Ke, X., Zhang, K., Wu, Q., 2021. High-efficiency TiO2/ZnO nanocomposites photocatalysts by sol–gel and hydrothermal methods. J. Sol-Gel Sci. Technol. 99, 92–100. https://doi.org/10.1007/s10971-021-05552-8

Bai, S., Yuan, Z., Gao, F., 2018. Synthesis, characterization and applications of ZnO/TiO2/SiO2 zinc (tris) thiourea sulfate nanocomposite. J. Mater. Chem. C 34, 3898–3904.

Banerjee, A.N., 2011. The design, fabrication, and photocatalytic utility of nanostructured semiconductors: Focus on TiO2-based nanostructures. Nanotechnol. Sci. Appl. 4, 35–65. https://doi.org/10.2147/NSA.S9040

Banerjee, A.N., Chattopadhyay, K.K., 2005. Recent developments in the emerging field of crystalline p-type transparent conducting oxide thin films. Prog. Cryst. Growth Charact. Mater. 50, 52–105. https://doi.org/10.1016/j.pcrysgrow.2005.10.001

Batista-Grau, P., Sánchez-Tovar, R., Fernández-Domene, R.M., García-Antón, J., 2020. Formation of ZnO nanowires by anodization under hydrodynamic conditions for photoelectrochemical water splitting. Surf. Coatings Technol. 381, 125197.

https://doi.org/10.1016/j.surfcoat.2019.125197

Benkara, S., Zerkout, S., 2010. Preparation and characterization of ZnO nanorods grown into aligned TiO 2 nanotube array. J. Mater. Environ. Sci. 1.

Blasco-Tamarit, E., Muñoz-Portero, M.J., Sánchez-Tovar, R., Fernández-Domene, R.M., García-Antón, J., 2018. The effect of Reynolds number on TiO2 nanosponges doped with Li+ cations. New J. Chem. 42, 11054–11063. https://doi.org/10.1039/c8nj00800k

Bonatto, F., Luisa Puga, M., Kopp Alves, A., Arguello da Silva, J., Lavayen Jimenez, V., Pérez Bergmann, C., 2020. Direct synthesis of singular silver dendrites over TiO2 nanotubes using pentetic acid as capping agent. Mater. Lett. 264, 127163. https://doi.org/10.1016/j.matlet.2019.127163

Boro, B., Gogoi, B., Rajbongshi, B.M., Ramchiary, A., 2018a. Nano-structured TiO2/ZnO nanocomposite for dye-sensitized solar cells application: A review. Renew. Sustain. Energy Rev. 81, 2264–2270. https://doi.org/10.1016/j.rser.2017.06.035

Boro, B., Gogoi, B., Rajbongshi, B.M., Ramchiary, A., 2018b. Nano-structured TiO2/ZnO nanocomposite for dye-sensitized solar cells application: A review. Renew. Sustain. Energy Rev. 81, 2264–2270. https://doi.org/https://doi.org/10.1016/j.rser.2017.06.035

Boyadjiev, S.I., Kéri, O., Bárdos, P., Firkala, T., Gáber, F., Nagy, Z.K., Baji, Z., Takács, M., Szilágyi, I.M., 2017. TiO 2 /ZnO and ZnO/TiO 2 core/shell nanofibers prepared by electrospinning and atomic layer deposition for photocatalysis and gas sensing. Appl. Surf. Sci. 424, 190–197. https://doi.org/10.1016/j.apsusc.2017.03.030

Brooms, T., Otieno, B., Onyango, M., Ochieng, A., 2017. Photocatalytic degradation of P-Cresol using TiO 2 /ZnO hybrid surface capped with polyaniline. J. Environ. Sci. Heal. Part A 53, 1–9. https://doi.org/10.1080/10934529.2017.1377583

Byrappa, K., Yoshimura, M., 2013. Handbook of Hydrothermal Technology, Handbook of Hydrothermal Technology. https://doi.org/10.1016/C2009-0-20354-0

Cao, Z., Yang, Y., Qin, J., He, J., Su, Z., 2022. 3D TiO 2 / ZnO hybrid framework : Stable host for lithium metal anodes. Chem. Eng. J. 427, 132026. https://doi.org/10.1016/j.cej.2021.132026

Chabalala, M.B., Gumbi, N.N., Mamba, B.B., Al-Abri, M.Z., Nxumalo, E.N., 2021. Photocatalytic Nanofiber Membranes for the Degradation of Micropollutants and Their Antimicrobial Activity: Recent Advances and Future Prospects. Membr. . https://doi.org/10.3390/membranes11090678

Chen, H., Zhu, L., Liu, H., Li, W., 2013. Effects of preparing conditions on the nanostructures electrodeposited from the Zn(NO3)2 electrolyte containing KCl. Thin Solid Films 534, 205–213. https://doi.org/10.1016/j.tsf.2013.02.060

Chen, Q., Tong, R., Chen, X., Xue, Y., Xie, Z., Kuang, Q., Zheng, L., 2018. Ultrafine ZnO quantum dot-modified TiO2 composite photocatalysts: The role of the quantum size effect in heterojunction-enhanced photocatalytic hydrogen evolution. Catal. Sci. Technol. 8, 1296–1303. https://doi.org/10.1039/c7cy02310c

Chen, X., Mao, S.S., 2007. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. Chem. Rev. 107, 2891–2959. https://doi.org/10.1021/cr0500535

Cheng, Z., Gu, Z., Chen, J., Yu, J., Zhou, L., 2016. Synthesis, characterization, and photocatalytic activity of porous La–N–co-doped TiO2 nanotubes for gaseous

chlorobenzene oxidation. J. Environ. Sci. (China). https://doi.org/10.1016/j.jes.2015.09.026

Choi, K.-S., Jang, H.S., McShane, C.M., Read, C.G., Seabold, J.A., 2010. Electrochemical synthesis of inorganic polycrystalline electrodes with controlled architectures. MRS Bull. 35, 753–760. https://doi.org/10.1557/mrs2010.504

Chu, D., Younis, A., Li, S., 2012. Direct growth of TiO 2 nanotubes on transparent substrates and their resistive switching characteristics. J. Phys. D. Appl. Phys. 45, 1–5. https://doi.org/10.1088/0022-3727/45/35/355306

Dai, S., Li, Y., Du, Z., Carter, K.R., 2013. Electrochemical Deposition of ZnO Hierarchical Nanostructures from Hydrogel Coated Electrodes. J. Electrochem. Soc. 160, D156–D162. https://doi.org/10.1149/2.064304jes

Degen, A., Kosec, M., 2000. Effect of pH and impurities on the surface charge of zinc oxide in aqueous solution. J. Eur. Ceram. Soc. 20, 667–673. https://doi.org/10.1016/S0955-2219(99)00203-4

Drunka, R., Grabis, J., Letlena, A., Jankovica, D., Krumina, A., Steins, I., 2019. Preparation of ZnO modified TiO2 nanoporous coatings and their photocatalytic properties. IOP Conf. Ser. Mater. Sci. Eng. 503. https://doi.org/10.1088/1757-899X/503/1/012008

Duarte, C.A., Goulart, L.R., Filice, letícia de S.C., De Lima, I.L., Campos-Fernándes, E., Dantas, N.O., Silva, A.C.A., Soares, M.B.P., Santos, R.R., CArdoso, C.M.A., França, L.S. de A., Rocha, V.P.C., Ribeiro, A. rosa L.P., Perez, G., Carvalho, L.N., Alonso-Goulart, V., 2020. Characterization of Crystalline Phase of TiO 2. Materials (Basel). 13, 4071.

El Ruby Mohamed, A., Rohani, S., 2011. Modified TiO2 nanotube arrays (TNTAs):

Progressive strategies towards visible light responsive photoanode, a review. Energy Environ. Sci. 4, 1065–1086. https://doi.org/10.1039/c0ee00488j

Elfiky, M., Salahuddin, N., 2021. Advanced sensing platform for nanomolar detection of food preservative nitrite in sugar byproducts based on 3D mesoporous nanorods of montmorillonite/TiO2–ZnO hybrids. Microchem. J. 170, 106582. https://doi.org/https://doi.org/10.1016/j.microc.2021.106582

Elias, J., Le, C., 2008. Electrochemical deposition of ZnO nanowire arrays with tailored dimensions 621, 171–177. https://doi.org/10.1016/j.jelechem.2007.09.015

Fakharuddin, A., Di Giacomo, F., Palma, A.L., Matteocci, F., Ahmed, I., Razza, S., D'Epifanio, A., Licoccia, S., Ismail, J., Di Carlo, A., Brown, T.M., Jose, R., 2015. Vertical TiO2 Nanorods as a Medium for Stable and High-Efficiency Perovskite Solar Modules. ACS Nano 9, 8420–8429. https://doi.org/10.1021/acsnano.5b03265

Farooq, U., Ahmed, F., Pervez, S.A., Rehman, S., Pope, M.A., Fichtner, M., Roberts, E.P.L., 2020. A stable TiO 2 –graphene nanocomposite anode with high rate capability for lithium-ion batteries . RSC Adv. 10, 29975–29982. https://doi.org/10.1039/d0ra05300g

Fatimah, I., Novitasari, 2016. Preparation of TiO2-ZnO and its activity test in sonophotocatalytic degradation of phenol. IOP Conf. Ser. Mater. Sci. Eng. 107. https://doi.org/10.1088/1757-899X/107/1/012003

Feldheim, D.L., Keating, C.D., 1998. Self-assembly of single electron transistors and related devices. Chem. Soc. Rev. 27, 1–12. https://doi.org/10.1039/a827001z

Feng, W., Lin, L., Li, H., Chi, B., Pu, J., Li, J., 2017. Hydrogenated TiO2/ZnO heterojunction nanorod arrays with enhanced performance for photoelectrochemical water splitting. Int. J. Hydrogen Energy 42, 3938–3946.

https://doi.org/10.1016/j.ijhydene.2016.10.087

Feng, W., Yang, X., He, Z., Liu, M., 2021. Hydrogen sulfide gas sensor based on TiO2–ZnO composite sensing membrane-coated no-core fiber. J. Phys. D. Appl. Phys. 54. https://doi.org/10.1088/1361-6463/abd503

Frade, T., Lobato, K., Carreira, J.F.C., Rodrigues, J., Monteiro, T., Gomes, A., 2016. TiO2 anatase intermediary layer acting as template for ZnO pulsed electrodeposition. Mater. Des. 110, 18–26. https://doi.org/10.1016/j.matdes.2016.07.122

Gaya, U.I., Abdullah, A.H., 2008. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. J. Photochem. Photobiol. C Photochem. Rev. 9, 1–12. https://doi.org/10.1016/j.jphotochemrev.2007.12.003

Georgakopoulos, T., Todorova, N., Pomoni, K., Trapalis, C., 2015. On the transient photoconductivity behavior of sol-gel TiO2/ZnO composite thin films. J. Non. Cryst. Solids 410, 135–141. https://doi.org/10.1016/j.jnoncrysol.2014.11.034

Ghicov, A., Schmuki, P., 2009. Self-ordering electrochemistry: A review on growth and functionality of TiO2 nanotubes and other self-aligned MOx structures. Chem. Commun. 2791–2808. https://doi.org/10.1039/b822726h

Giannakopoulou, T., Todorova, N., Giannouri, M., Yu, J., Trapalis, C., 2014. Optical and photocatalytic properties of composite TiO 2 / ZnO thin films. Catal. Today 230, 174–180. https://doi.org/10.1016/j.cattod.2013.10.003

Gong, D., Grimes, C.A., Varghese, O.K., 2001. Titanium oxide nanotube arrays prepared by anodic oxidation 1, 3331–3334.

Goux, A., Pauporté, T., Chivot, J., Lincot, D., 2005. Temperature effects on ZnO

electrodeposition. Electrochim. Acta 50, 2239–2248. https://doi.org/10.1016/j.electacta.2004.10.007

Guo, L., Gao, G., Liu, X., Liu, F., 2008. Preparation and characterization of TiO2 nanosponge. Mater. Chem. Phys. 111, 322–325. https://doi.org/10.1016/j.matchemphys.2008.04.016

Gupta, D., Chauhan, R., Kumar, N., Singh, V., Srivastava, V.C., Mohanty, P., Mandal, T.K., 2020. Enhancing photocatalytic degradation of quinoline by ZnO:TiO2 mixed oxide: Optimization of operating parameters and mechanistic study. J. Environ. Manage. 258, 110032. https://doi.org/10.1016/j.jenvman.2019.110032

Hashem, A.M., Abdal-hay, A., 2021. Synthesis of TiO2@ZnO heterojunction for dye photodegradation and wastewater treatment. J. Alloys Compd. 886, 161169. https://doi.org/10.1016/j.jallcom.2021.161169

Hashemi, M.M., Nikfarjam, A., Hajghassem, H., Salehifar, N., 2020. Hierarchical Dense Array of ZnO Nanowires Spatially Grown on ZnO/TiO2 Nanofibers and Their Ultraviolet Activated Gas Sensing Properties. J. Phys. Chem. C. https://doi.org/10.1021/acs.jpcc.9b07207

Hernández, S., Hidalgo, D., Sacco, A., Chiodoni, A., Lamberti, A., Cauda, V., Tresso, E., Saracco, G., 2015. Comparison of photocatalytic and transport properties of TiO2 and ZnO nanostructures for solar-driven water splitting. Phys. Chem. Chem. Phys. 17, 7775–7786. https://doi.org/10.1039/c4cp05857g

Hidayat, R., Fadillah, G., Wahyuningsih, S., 2019. A control of TiO2 nanostructures by hydrothermal condition and their application: A short review. IOP Conf. Ser. Mater. Sci. Eng. 578. https://doi.org/10.1088/1757-899X/578/1/012031

Himmah, S.W., Diantoro, M., Astarini, N.A., Tiana, S.K.G., Nasikhudin, Hidayat, A.,

Taufiq, A., 2021. Structural, morphological, optical, and electrical properties of TiO2/ZnO rods multilayer films as photoanode on dye-sensitized solar cells. J. Phys. Conf. Ser. 1816. https://doi.org/10.1088/1742-6596/1816/1/012095

Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W., 1995. Environmental Applications of Semiconductor Photocatalysis. Chem. Rev. 95, 69–96. https://doi.org/10.1021/cr00033a004

Hoyer, P., 1996. Formation of a titanium dioxide nanotube array. Langmuir. https://doi.org/10.1021/la9507803

Hsu, C.-L., Wu, H.-Y., Fang, C.-C., Chang, S.-P., 2018. Solution-Processed UV and Visible Photodetectors Based on Y-Doped ZnO Nanowires with TiO2 Nanosheets and Au Nanoparticles. ACS Appl. Energy Mater. 1, 2087–2095. https://doi.org/10.1021/acsaem.8b00180

Huang, J.Y., Zhang, K.Q., Lai, Y.K., 2013. Fabrication, modification, and emerging applications of TiO2 nanotube arrays by electrochemical synthesis: A review. Int. J. Photoenergy 2013. https://doi.org/10.1155/2013/761971

Ii, W.W., 2000. Coatings 7.1. https://doi.org/10.1016/B978-0-7506-5924-6.50008-8

Iijima, S., Ichihashi, T., 1993. Single-shell carbon nanotubes of 1-nm diameter. Nature 363, 603–605. https://doi.org/10.1038/363603a0

Inamdar, A.I., Mujawar, S.H., Barman, S.R., Bhosale, P.N., Patil, P.S., 2008. The effect of bath temperature on the electrodeposition of zinc oxide thin films via an acetate medium. Semicond. Sci. Technol. 23, 085013. https://doi.org/10.1088/0268-1242/23/8/085013

Inamdar, A.I., Sonavane, A.C., Sharma, S.K., Im, H., Patil, P.S., 2010. Nanocrystalline zinc oxide thin films by novel double pulse single step electrodeposition. J. Alloys

Compd. 495, 76–81. https://doi.org/10.1016/j.jallcom.2010.01.090

Indira, K., Mudali, U.K., Nishimura, T., Rajendran, N., 2015. A Review on TiO2 Nanotubes: Influence of Anodization Parameters, Formation Mechanism, Properties, Corrosion Behavior, and Biomedical Applications. J. Bio- Tribo-Corrosion 1, 1–22. https://doi.org/10.1007/s40735-015-0024-x

Indora, V., Yadav, S., Mohan, D., 2020. Optical and structural analysis of sol-gel derived TiO2/MWCNT nanocomposites. 3Rd Int. Conf. Condens. Matter Appl. Phys. 2220, 020110. https://doi.org/10.1063/5.0001850

Iqbal, A., Saidu, U., Sreekantan, S., Ahmad, M.N., Rashid, M., 2021. Mesoporous TiO 2 Implanted ZnO QDs for the. Materials (Basel). 1–21.

Izaki, M., Omi, T., 1996. Transparent zinc oxide films prepared by electrochemical reaction. Appl. Phys. Lett. 68, 2439–2440. https://doi.org/10.1063/1.116160

Jain, R., Jadon, N., Pawaiya, A., 2017. Polypyrrole Based Next Generation Electrochemical Sensors and Biosensors: A Review. TrAC Trends Anal. Chem. 97. https://doi.org/10.1016/j.trac.2017.10.009

Jiang, Q., Han, Z., Yuan, Y., Cai, C., Li, J., Cheng, Z., 2022. Controlled preparation and photocatalytic performance of TiO2/ZnO phase-mixed nanotubes-based nano-spheres. Mater. Chem. Phys. 279, 125737. https://doi.org/10.1016/j.matchemphys.2022.125737

Jiang, S., Wu, M., Zhou, Y., Wen, Y., Yang, C., Zhang, S., 2007. Effects of electrodeposition conditions on the microstructures of ZnO thin films, in: Integrated Ferroelectrics. https://doi.org/10.1080/10584580601098563

Jiang, X., Xu, L., Ji, W., Wang, W., Du, J., Yang, L., Song, W., Han, X., Zhao, B., 2022. One plus one greater than Two: Ultrasensitive Surface-Enhanced Raman

scattering by TiO2/ZnO heterojunctions based on Electron-Hole separation. Appl. Surf. Sci. 584, 152609. https://doi.org/10.1016/j.apsusc.2022.152609

Kanjwal, M.A., Barakat, N.A.M., Sheikh, F.A., Kim, H.Y., 2010. Electrospun Titania Oxide Nanofibers Coupled Zinc Oxide Nanobranches as a Novel Nanostructure for Lithium Ion Batteries Applications Electrospun Titania Oxide Nanofibers Coupled Zinc Oxide Nanobranches as a Novel Nanostructure for Lithium Ion. https://doi.org/10.4303/bda/D110129

Karuppuchamy, S., Ito, S., 2008. Cathodic electrodeposition of nanoporous ZnO thin films from new electrochemical bath and their photoinduced hydrophilic properties. Vacuum 82, 547–550. https://doi.org/10.1016/j.vacuum.2007.06.002

Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T., Niihara, K., 1999. Titania nanotubes prepared by chemical processing. Adv. Mater. https://doi.org/10.1002/(SICI)1521-4095(199910)11:15<1307::AID-ADMA1307>3.0.CO;2-H

Kenanakis, G., Vernardou, D., Dalamagkas, A., Katsarakis, N., 2015. Photocatalytic and electrooxidation properties of TiO2 thin films deposited by sol-gel. Catal. Today 240, 146–152. https://doi.org/10.1016/j.cattod.2014.05.007

Khosravi, M., Maddah, A., Mehrdadi, N., Nabi, R., Baghdadi, M., 2020. Synthesis of TiO 2 /ZnO electrospun nanofibers coated-sewage sludge carbon for adsorption of Ni(II), Cu(II), and COD from aqueous solutions and industrial wastewaters Synthesis of TiO 2 /ZnO electrospun nanofibers coated-sewage sludge carbon for adsorptio. J. Dispers. Sci. Technol.

Kianfar, A., Arayesh, M.A., 2019. Synthesis, characterization and investigation of photocatalytic and catalytic applications of Fe3O4/TiO2/CuO nanoparticles for degradation of MB and reduction of nitrophenols. J. Environ. Chem. Eng. 8,

103640. https://doi.org/10.1016/j.jece.2019.103640

Klein, D.L., Rotht, R., Lim, A.K.L., Alivisatosti, A.P., McEuen, P.L., 1997. A single-electron transistor made from a cadmium selenide nanocrystal. Nature 389, 699–701. https://doi.org/10.1038/39535

Kochuveedu, S.T., 2016. Photocatalytic and Photoelectrochemical Water Splitting on TiO 2 via Photosensitization 2016.

Kubiak, A., Bielan, Z., Kubacka, M., Gabała, E., Zgoła-Grześkowiak, A., Janczarek, M., Zalas, M., Zielinska-Jurek, A., Siwińska-Ciesielczyk, K., Jesionowski, T., 2020. Microwave-assisted synthesis of a TiO2-CuO heterojunction with enhanced photocatalytic activity against tetracycline. Appl. Surf. Sci. 520, 146344. https://doi.org/10.1016/j.apsusc.2020.146344

Kubiak, A., Żółtowska, S., Bartkowiak, A., Gabała, E., Sacharczuk, N., Zalas, M., Siwińska-Ciesielczyk, K., Jesionowski, T., 2021. The TiO2-ZnO Systems with Multifunctional Applications in Photoactive Processes—Efficient Photocatalyst under UV-LED Light and Electrode Materials in DSSCs. Mater. . https://doi.org/10.3390/ma14206063

Kuchibhatla, S.V.N.T., Karakoti, A.S., Bera, D., Seal, S., 2007. One dimensional nanostructured materials. Prog. Mater. Sci. 52, 699–913. https://doi.org/10.1016/j.pmatsci.2006.08.001

Kumar, M., Sasikumar, C., 2014. Electrodeposition of Nanostructured ZnO Thin Film : A Review 2, 18–23. https://doi.org/10.12691/ajmse-2-2-2

Kusior, A., Wnuk, A., Trenczek-Zajac, A., Zakrzewska, K., Radecka, M., 2015. TiO2 nanostructures for photoelectrochemical cells (PECs). Int. J. Hydrogen Energy 40, 4936–4944. https://doi.org/10.1016/j.ijhydene.2015.01.103

Kusior, A., Zych, L., Zakrzewska, K., Radecka, M., 2019. Photocatalytic activity of TiO 2 /SnO 2 nanostructures with controlled dimensionality/complexity. Appl. Surf. Sci. 471, 973–985. https://doi.org/10.1016/j.apsusc.2018.11.226

Kutuzova, A., Dontsova, T., Kwapinski, W., 2020. TiO2–SnO2 Nanocomposites: Effect of Acid–Base and Structural-Adsorption Properties on Photocatalytic Performance. J. Inorg. Organomet. Polym. Mater. 30. https://doi.org/10.1007/s10904-020-01467-z

Lai, Y., Zhuang, H., Sun, L., Chen, Z., Lin, C., 2009. Self-organized TiO2 nanotubes in mixed organic-inorganic electrolytes and their photoelectrochemical performance. Electrochim. Acta 54, 6536–6542. https://doi.org/10.1016/j.electacta.2009.06.029

Lai, Y., Zhuang, H., Xie, K., Gong, D., Tang, Y., Sun, L., Lin, C., Chen, Z., 2010. Fabrication of uniform Ag/TiO2 nanotube array structures with enhanced photoelectrochemical performance. New J. Chem. 34, 1335–1340. https://doi.org/10.1039/b9nj00780f

Le, P.H., Leu, J., 2018. Recent Advances in TiO2 Nanotube-Based Materials for Photocatalytic Applications Designed by Anodic Oxidation, in: Titanium Dioxide - Material for a Sustainable Environment. https://doi.org/10.5772/intechopen.77063

Lee, C.G., Na, K.H., Kim, W.T., Park, D.C., Yang, W.H., Choi, W.Y., 2019. TiO2/ZnO nanofibers prepared by electrospinning and their photocatalytic degradation of methylene blue compared with TiO2 nanofibers. Appl. Sci. 9. https://doi.org/10.3390/app9163404

Lee, K.M., Lee, E.S., Yoo, B., Shin, D.H., 2013. Synthesis of ZnO-decorated TiO2nanotubes for dye-sensitized solarcells. Electrochim. Acta 109, 181–186. https://doi.org/10.1016/j.electacta.2013.07.055

Li, F., Jiao, Y., Xie, S., Li, J., 2015. Sponge-like porous TiO2/ZnO nanodonuts for high efficiency dye-sensitized solar cells. J. Power Sources 280, 373–378. https://doi.org/10.1016/j.jpowsour.2015.01.118

Li, S., Zhang, G., Guo, D., Yu, L., Zhang, W., 2009. Anodization fabrication of highly ordered TiO2 nanotubes. J. Phys. Chem. C 113, 12759–12765. https://doi.org/10.1021/jp903037f

Li, Y., Zhao, Q., Shen, Y., Liu, X., Zhao, H., Jiang, T., 2017. Fabrication of a Ternary TiO 2 –CuO/Graphite Oxide Composite and Its Efficient Application in Photocatalysis. J. Nanosci. Nanotechnol. 17, 3194–3199. https://doi.org/10.1166/jnn.2017.13048

Li, Z., Yu, L., Wang, H., Yang, H., Ma, H., 2020. Tio2 passivation layer on ZnO hollow microspheres for quantum dots sensitized solar cells with ron collection. Nanomaterials 10, 1–14. https://doi.org/10.3390/nano10040631

Liang, Z., Gao, R., Lan, J., Wiranwetchayan, O., Zhang, Q., 2013. Solar Energy Materials & Solar Cells Growth of vertically aligned ZnO nanowalls for inverted polymer solar cells. Sol. Energy Mater. Sol. Cells 117, 34–40. https://doi.org/10.1016/j.solmat.2013.05.019

Liao, Y., Zhang, K., Wang, X., Zhang, D., Li, Y., Su, H., Zhang, H., Zhong, Z., 2018. Preparation of ZnO@TiO2 nanotubes heterostructured film by thermal decomposition and their photocatalytic performances. RSC Adv. 8, 8064–8070. https://doi.org/10.1039/c7ra13222k

Lin, L., Yang, Y., Men, L., Wang, X., He, D., Chai, Y., Zhao, B., Ghoshroy, S., Tang, Q., 2013. A highly efficient TiO2@ZnO n-p-n heterojunction nanorod photocatalyst. Nanoscale 5, 588–593. https://doi.org/10.1039/c2nr33109h

Lin, W.H., Chiu, Y.H., Shao, P.W., Hsu, Y.J., 2016. Metal-Particle-Decorated ZnO Nanocrystals: Photocatalysis and Charge Dynamics. ACS Appl. Mater. Interfaces 8, 32754–32763. https://doi.org/10.1021/acsami.6b08132

Lin, Y., Yang, J., Zhou, X., 2011. Controlled synthesis of oriented ZnO nanorod arrays by seed-layer-free electrochemical deposition. Appl. Surf. Sci. 258, 1491–1494. https://doi.org/10.1016/j.apsusc.2011.09.113

Liu, C., Jiao, Y., Tian, Y., Wang, Y., Jiang, Z., 2013. Biomimetic Synthesis of TiO2-SiO2-Ag Nanocomposites with Enhanced Visible-Light Photocatalytic Activity. ACS Appl. Mater. Interfaces 5. https://doi.org/10.1021/am4004733

Liu, W., Su, P., Chen, S., Wang, N., Ma, Y., Liu, Y., Wang, J., Zhang, Z., Li, H., Webster, T.J., 2014. Synthesis of TiO2 nanotubes with ZnO nanoparticles to achieve antibacterial properties and stem cell compatibility. Nanoscale 6, 9050–9062. https://doi.org/10.1039/c4nr01531b

Liu, X., Cheng, S., Liu, H., Hu, S., Zhang, D., Ning, H., 2012. A survey on gas sensing technology. Sensors (Switzerland) 12, 9635–9665. https://doi.org/10.3390/s120709635

Liu, Y., Cai, T., Wang, L., Shuqu, Z., Zhang, G., Xia, X., 2017. Hollow Microsphere TiO 2 /ZnO p–n Heterojuction with High Photocatalytic Performance for 2,4-Dinitropheno Mineralization. Nano 12. https://doi.org/10.1142/S179329201750076X

Lou, Y., Yuan, S., Zhao, Y., Hu, P., Wang, Z., Zhang, M., Shi, L., Li, D., 2013. A simple route for decorating TiO2 nanoparticle over ZnO aggregates dye-sensitized solar cell. Chem. Eng. J. 229, 190–196. https://doi.org/10.1016/j.cej.2013.06.006

Lu, J., Jin, H., Dai, Y., Yang, K., Huang, B., 2012. Effect of Electronegativity and

Charge Balance on the Visible-Light-Responsive Photocatalytic Activity of Nonmetal Doped Anatase TiO_2. Int. J. Photoenergy 2012, 928503. https://doi.org/10.1155/2012/928503

Lü, X., Huang, F., Mou, X., Wang, Y., Xu, F., 2010. A general preparation strategy for hybrid TiO2 hierarchical spheres and their enhanced solar energy utilization efficiency. Adv. Mater. 22, 3719–3722. https://doi.org/10.1002/adma.201001008

Lv, Y., Guo, Y., Zhang, H., Zhou, X., Chen, H., 2018. Enhanced efficiency and stability of fully air-processed TiO2 nanorods array based perovskite solar cell using commercial available CuSCN and carbon. Sol. Energy 173, 7–16. https://doi.org/10.1016/j.solener.2018.07.057

Ma, Q. lan, Ma, S., Huang, Y.M., 2018. Enhanced photovoltaic performance of dye sensitized solar cell with ZnO nanohoneycombs decorated TiO2 photoanode. Mater. Lett. 218, 237–240. https://doi.org/10.1016/j.matlet.2018.02.028

MacAk, J.M., Sirotna, K., Schmuki, P., 2005. Self-organized porous titanium oxide prepared in Na2SO 4/NaF electrolytes. Electrochim. Acta 50, 3679–3684. https://doi.org/10.1016/j.electacta.2005.01.014

Macák, J.M., Tsuchiya, H., Schmuki, P., 2005. High-aspect-ratio TiO2 nanotubes by anodization of titanium. Angew. Chemie - Int. Ed. 44, 2100–2102. https://doi.org/10.1002/anie.200462459

Macak, J.M., Zlamal, M., Krysa, J., Schmuki, P., 2007. Self-organized TiO2 nanotube layers as highly efficient photocatalysts. Small 3, 300–304. https://doi.org/10.1002/smll.200600426

Madian, M., Eychmüller, A., Giebeler, L., 2018. Current Advances in TiO 2 -Based Nanostructure Electrodes for High Performance Lithium Ion Batteries.

https://doi.org/10.3390/batteries4010007

Malallah Rzaij, J., Mohsen Abass, A., 2020. Review on: TiO2 Thin Film as a Metal Oxide Gas Sensor. J. Chem. Rev. 2, 114–121. https://doi.org/10.33945/sami/jcr.2020.2.4

Mane, R.S., Lee, W.J., Pathan, H.M., Han, S.H., 2005. Nanocrystalline TiO2/ZnO thin films: Fabrication and application to dye-sensitized solar cells. J. Phys. Chem. B 109, 24254–24259. https://doi.org/10.1021/jp0531560

Mansoorianfar, M., Rahighi, R., Hojjati-Najafabadi, A., Mei, C., Li, D., 2021. Amorphous/crystalline phase control of nanotubular TiO2 membranes via pressure-engineered anodizing. Mater. Des. 198, 109314. https://doi.org/10.1016/j.matdes.2020.109314

Marimuthu, T., Anandhan, N., 2017. Growth and characterization of ZnO nanostructure on TiO2-ZnO films as a light scattering layer for dye sensitized solar cells. Mater. Res. Bull. 95, 616–624. https://doi.org/10.1016/j.materresbull.2017.04.051

Marotti, R.E., Giorgi, P., Machado, G., Dalchiele, E.A., 2006. Crystallite size dependence of band gap energy for electrodeposited ZnO grown at different temperatures. Sol. Energy Mater. Sol. Cells 90, 2356–2361. https://doi.org/10.1016/j.solmat.2006.03.008

Maziarz, W., Kusior, A., Trenczek-Zajac, A., 2016. Nanostructured TiO2-based gas sensors with enhancedsensitivity to reducing gases. Beilstein J. Nanotechnol. 7, 1718–1726. https://doi.org/10.3762/BJNANO.7.164

Mendoza, C., Valle, A., Castellote, M., Bahamonde, A., Faraldos, M., 2014. TiO2 and TiO2 –SiO2 coated cement: Comparison of mechanic and photocatalytic properties. Appl. Catal. B Environ. 178, 155–164.

https://doi.org/10.1016/j.apcatb.2014.09.079

Mercado, C., Lubrin, M., Hernandez, H., Carubio, R., 2019. Comparison of Photoelectrochemical Current in Amorphous and Crystalline Anodized TiO 2 Nanotube Electrodes. Int. J. Photoenergy 2019, 1–8. https://doi.org/10.1155/2019/9848740

Michalcik, Z., Horakova, M., Spatenka, P., Klementova, S., Zlamal, M., Martin, N., 2012. Photocatalytic activity of nanostructured titanium dioxide thin films. Int. J. Photoenergy 2012. https://doi.org/10.1155/2012/689154

Miyoshi, A., Nishioka, S., Maeda, K., 2018. Water Splitting on Rutile TiO2-Based Photocatalysts. Chem. - A Eur. J. 24. https://doi.org/10.1002/chem.201800799

Mohsen, M., Yousef, M., 2015. Visible light-driven photoelectrochemical water splitting on ZnO – TiO 2 heterogeneous nanotube photoanodes. J. Appl. Electrochem. 557–566. https://doi.org/10.1007/s10800-015-0836-x

Mor, G.K., Shankar, K., Paulose, M., Varghese, O.K., Grimes, C.A., 2006a. Use of highly-ordered TiO 2 nanotube arrays in dye-sensitized solar cells. Nano Lett. 6, 215–218. https://doi.org/10.1021/nl052099j

Mor, G.K., Shankar, K., Paulose, M., Varghese, O.K., Grimes, C.A., 2005. Enhanced photocleavage of water using titania nanotube arrays. Nano Lett. 5, 191–195. https://doi.org/10.1021/nl048301k

Mor, G.K., Varghese, O.K., Paulose, M., Mukherjee, N., Grimes, C.A., 2003. Fabrication of tapered, conical-shaped titania nanotubes. J. Mater. Res. 18, 2588–2593. https://doi.org/10.1557/JMR.2003.0362

Mor, G.K., Varghese, O.K., Paulose, M., Shankar, K., Grimes, C.A., 2006b. A review on highly ordered, vertically oriented TiO2 nanotube arrays: Fabrication, material

properties, and solar energy applications. Sol. Energy Mater. Sol. Cells 90, 2011–2075. https://doi.org/10.1016/j.solmat.2006.04.007

Moradi, S., Aberoomand-Azar, P., Raeis-Farshid, S., Abedini-Khorrami, S., Givianrad, M.H., 2016. The effect of different molar ratios of ZnO on characterization and photocatalytic activity of TiO2/ZnO nanocomposite. J. Saudi Chem. Soc. 20, 373–378. https://doi.org/10.1016/j.jscs.2012.08.002

Nagamine, S., 2020. Photocatalytic microreactor using TiO2/Ti plates: Formation of TiO2 nanostructure and separation of oxidation/reduction into different channels. Adv. Powder Technol. 31, 521–527. https://doi.org/10.1016/j.apt.2019.11.008

Nan, Y., 2013. A review of Nanostructured TiO 2 Application in Li-Ion Batteries Jiang Wei 1, 752, 301–306. https://doi.org/10.4028/www.scientific.net/AMR.750-752.301

Naseri, N., Yousefi, M., Moshfegh, A.Z., 2011. A comparative study on photoelectrochemical activity of ZnO/TiO2 and TiO2/ZnO nanolayer systems under visible irradiation. Sol. Energy 85, 1972–1978. https://doi.org/10.1016/j.solener.2011.05.002

Ng, S., Kuberský, P., Krbal, M., Prikryl, J., Gärtnerová, V., Moravcová, D., Sopha, H., Zazpe, R., Yam, F.K., Jäger, A., Hromádko, L., Beneš, L., Hamáček, A., Macak, J.M., 2018. ZnO Coated Anodic 1D TiO2 Nanotube Layers: Efficient Photo-Electrochemical and Gas Sensing Heterojunction. Adv. Eng. Mater. https://doi.org/10.1002/adem.201700589

Ng, S.W., Yam, F.K., Hassan, Z., 2015. Rapid formation of zinc oxide nanosheets on titanium dioxide nanotubes through electrochemical method. Optoelectron. Adv. Mater. Rapid Commun. 9, 1429–1434.

Ni, M., Leung, M.K.H., Leung, D.Y.C., Sumathy, K., 2007. A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production. Renew. Sustain. Energy Rev. 11, 401–425. https://doi.org/10.1016/j.rser.2005.01.009

Odhiambo, V., Ongarbayeva, A., Kéri, O., Simon, L., Szilágyi, I., 2020. Synthesis of TiO2/WO3 Composite Nanofibers by a Water-Based Electrospinning Process and Their Application in Photocatalysis. Nanomaterials 10, 882. https://doi.org/10.3390/nano10050882

Oliveira, H.G., Silva, E.D., Longo, C., 2010. Electrochemical and photocatalytic properties of TiO 2 /WO 3 photoelectrodes. Sol. Hydrog. Nanotechnol. V 7770, 777006. https://doi.org/10.1117/12.860804

Opra, D.P., Gnedenkov, S. V, Sinebryukhov, S.L., 2019. Recent efforts in design of TiO 2 (B) anodes for high-rate lithium-ion batteries : A review. J. Power Sources 442, 227225. https://doi.org/10.1016/j.jpowsour.2019.227225

Ostojic, J., Herenda, S., Bešić, Z., Milos, M., Galic, B., 2017. Advantages of an Electrochemical Method Compared to the Spectrophotometric Kinetic Study of Peroxidase Inhibition by Boroxine Derivative. Molecules 22, 1120. https://doi.org/10.3390/molecules22071120

Otani, S., Katayama, J., Umemoto, H., Matsuoka, M., 2006. Effect of Bath Temperature on the Electrodeposition Mechanism of Zinc Oxide Film from Zinc Nitrate Solution. J. Electrochem. Soc. 153, C551. https://doi.org/10.1149/1.2205187

Palmas, S., Polcaro, A.M., Ruiz, J.R., Da Pozzo, A., Mascia, M., Vacca, A., 2010. TiO2 photoanodes for electrically enhanced water splitting. Int. J. Hydrogen Energy 35, 6561–6570. https://doi.org/10.1016/j.ijhydene.2010.04.039

Pantelis, D., Tsiourva, T., 2017. 10. Corrosion of weldments, in: Trends in Oil and Gas Corrosion Research and Technologies: Production and Transmission. https://doi.org/10.1016/B978-0-08-101105-8.00010-3

Paramasivam, I., Jha, H., Liu, N., Schmuki, P., 2012. A review of photocatalysis using self-organized TiO2 nanotubes and other ordered oxide nanostructures. Small 8, 3073–3103. https://doi.org/10.1002/smll.201200564

Park, J.Y., Choi, S.W., Lee, J.W., Lee, C., Kim, S.S., 2009. Synthesis and gas sensing properties of TiO2-ZnO core-shell nanofibers. J. Am. Ceram. Soc. 92, 2551–2554. https://doi.org/10.1111/j.1551-2916.2009.03270.x

Park, S., Lim, S.J., Kim, J., Yu, J.-W., 2017. Organic light-emitting diodes with an internal light extraction layer prepared by intense pulsed light. Macromol. Res. 25, 1022–1027. https://doi.org/10.1007/s13233-017-5140-7

Pérez-González, M., Tomás, S.A., Morales-Luna, M., Arvizu, M.A., Tellez-Cruz, M.M., 2015. Optical, structural, and morphological properties of photocatalytic TiO2-ZnO thin films synthesized by the sol-gel process. Thin Solid Films 594, 304–309. https://doi.org/10.1016/j.tsf.2015.04.073

Polsongkram, D., Chamninok, P., Pukird, S., Chow, L., Lupan, O., Chai, G., Khallaf, H., Park, S., Schulte, A., 2008. Effect of synthesis conditions on the growth of ZnO nanorods via hydrothermal method. Phys. B Condens. Matter 403, 3713–3717. https://doi.org/10.1016/j.physb.2008.06.020

Prabakaran, S., Nisha, K.D., Harish, S., Archana, J., Navaneethan, M., Ponnusamy, S., Muthamizhchelvan, C., Ikeda, H., Hayakawa, Y., 2019. Synergistic effect and enhanced electrical properties of TiO2/SnO2/ZnO nanostructures as electron extraction layer for solar cell application. Appl. Surf. Sci. 498.

https://doi.org/10.1016/j.apsusc.2019.143702

Pradhan, D., Leung, K.T., 2008. Controlled Growth of Two-Dimensional and One-Dimensional ZnO Nanostructures on Indium Tin Oxide Coated Glass by Direct Electrodeposition 9707–9716.

Pradhan, D., Sindhwani, S., Leung, K.T., 2010. Parametric Study on Dimensional Control of ZnO Nanowalls and Nanowires by Electrochemical Deposition 1727–1736. https://doi.org/10.1007/s11671-010-9702-2

Prakasam, H.E., Shankar, K., Paulose, M., Varghese, O.K., Grimes, C.A., 2007. A new benchmark for TiO2 nanotube array growth by anodization. J. Phys. Chem. C 111, 7235–7241. https://doi.org/10.1021/jp070273h

Prasad, B.E., Kamath, P.V., Ranganath, S., 2012. Electrodeposition of ZnO coatings from aqueous Zn (NO 3) 2 baths : effect of Zn concentration , deposition temperature , and time on orientation 3715–3722. https://doi.org/10.1007/s10008-012-1804-6

Prasannalakshmi, P., Shanmugam, N., 2017. Fabrication of TiO2/ZnO nanocomposites for solar energy driven photocatalysis. Mater. Sci. Semicond. Process. 61, 114–124. https://doi.org/10.1016/j.mssp.2017.01.008

Qin, J., Cao, Z., He, J., Li, H., Su, Z., 2021a. Fast fabrication of small pore anodic titania nanotube arrays under high voltage. Surf. Coatings Technol. 420, 127360. https://doi.org/https://doi.org/10.1016/j.surfcoat.2021.127360

Qin, J., Cao, Z., Li, H., Su, Z., 2021b. Formation of anodic TiO2 nanotube arrays with ultra-small pore size. Surf. Coatings Technol. 405, 126661. https://doi.org/10.1016/j.surfcoat.2020.126661

Qin, L., Chen, Q., Lan, R., Jiang, R., Quan, X., Xu, B., Zhang, F., Jia, Y., 2015. Effect

of Anodization Parameters on Morphology and Photocatalysis Properties of TiO2 Nanotube Arrays. J. Mater. Sci. Technol. 31. https://doi.org/10.1016/j.jmst.2015.07.012

Ramgir, N., Bhusari, R., Rawat, N.S., Patil, S.J., Debnath, A.K., Gadkari, S.C., Muthe, K.P., 2020. TiO2/ZnO heterostructure nanowire based NO2 sensor. Mater. Sci. Semicond. Process. 106. https://doi.org/10.1016/j.mssp.2019.104770

Reddy, C.V., Reddy, K.R., Shetti, N.P., Shim, J., Aminabhavi, T.M., Dionysiou, D.D., 2020. Hetero-nanostructured metal oxide-based hybrid photocatalysts for enhanced photoelectrochemical water splitting – A review. Int. J. Hydrogen Energy 45, 18331–18347. https://doi.org/10.1016/j.ijhydene.2019.02.109

Reyes-Coronado, D., Rodriguez Gattorno, G., Espinosa Pesqueira, M., Cab, C., de Coss, R., Oskam, G., 2008. Phase-Pure TiO2 Nanoparticles: Anatase, Brookite and Rutile. Nanotechnology 19, 145605. https://doi.org/10.1088/0957-4484/19/14/145605

Roduner, E., 2006. Size matters: Why nanomaterials are different. Chem. Soc. Rev. 35, 583–592. https://doi.org/10.1039/b502142c

Roy, P., Berger, S., Schmuki, P., 2011. TiO2 nanotubes: Synthesis and applications. Angew. Chemie - Int. Ed. 50, 2904–2939. https://doi.org/10.1002/anie.201001374

Samadipakchin, P., Mortaheb, H.R., Zolfaghari, A., 2017. ZnO nanotubes: Preparation and photocatalytic performance evaluation. J. Photochem. Photobiol. A Chem. 337, 91–99. https://doi.org/10.1016/j.jphotochem.2017.01.018

Sánchez-Tovar, R., Blasco-Tamarit, E., Fernández-Domene, R.M., Lucas-Granados, B., García-Antón, J., 2017. Should TiO2 nanostructures doped with Li+ be used as photoanodes for photoelectrochemical water splitting applications? J. Catal. 349,

41–52. https://doi.org/10.1016/j.jcat.2017.03.001

Sánchez-Tovar, R., Blasco-Tamarit, E., Fernández-Domene, R.M., Villanueva-Pascual, M., García-Antón, J., 2020. Electrochemical formation of novel TiO2-ZnO hybrid nanostructures for photoelectrochemical water splitting applications. Surf. Coatings Technol. 388, 125605. https://doi.org/10.1016/j.surfcoat.2020.125605

Sánchez-Tovar, R., Fernández-Domene, R.M., García-García, D.M., García-Antón, J., 2015a. Enhancement of photoelectrochemical activity for water splitting by controlling hydrodynamic conditions on titanium anodization. J. Power Sources 286, 224–231. https://doi.org/10.1016/j.jpowsour.2015.03.174

Sánchez-Tovar, R., Fernández-Domene, R.M., Martínez-Sánchez, A., Blasco-Tamarit, E., García-Antón, J., 2015b. Synergistic effect between hydrodynamic conditions during Ti anodization and acidic treatment on the photoelectric properties of TiO2 nanotubes. J. Catal. 330, 434–441. https://doi.org/10.1016/j.jcat.2015.08.002

Sanchez-Tovar, R., Lee, K., Garcia-Anton, J., Schmuki, P., 2013. Photoelectrochemical Poperties of Anodic TiO2 Nanosponge Layers. Ecs Electrochem. Lett. 2, H9–H11. https://doi.org/Doi 10.1149/2.005303eel

Sánchez-Tovar, R., Lee, K., García-Antón, J., Schmuki, P., 2013. Formation of anodic TiO2 nanotube or nanosponge morphology determined by the electrolyte hydrodynamic conditions. Electrochem. commun. 26, 1–4. https://doi.org/10.1016/j.elecom.2012.09.041

Sánchez-Tovar, R., Paramasivam, I., Lee, K., Schmuki, P., 2012. Influence of hydrodynamic conditions on growth and geometry of anodic TiO2 nanotubes and their use towards optimized DSSCs. J. Mater. Chem. 22, 12792. https://doi.org/10.1039/c2jm31246h

Shaheen, B.S., Salem, H.G., El-sayed, M.A., Allam, N.K., 2013. Thermal / Electrochemical Growth and Characterization of One- Dimensional ZnO / TiO 2 Hybrid Nanoelectrodes for Solar Fuel Production.

Shao, D., Sun, H., Xin, G., Lian, J., Sawyer, S., 2014. High quality ZnO–TiO2 core–shell nanowires for efficient ultraviolet sensing. Appl. Surf. Sci. 314, 872–876. https://doi.org/https://doi.org/10.1016/j.apsusc.2014.06.182

Sharma, S., Kumar, N., Makgwane, P., Chauhan, N., Kumari, K., Rani, M., Maken, S., 2021. TiO2/SnO2 nano-composite: New insights in synthetic, structural, optical and photocatalytic aspects. Inorganica Chim. Acta 529, 120640. https://doi.org/10.1016/j.ica.2021.120640

Sivaprakash, V., Narayanan, R., 2020. Synthesis of TiO2 nanotubes via electrochemical anodization with different water content. Mater. Today Proc. 37, 142–146. https://doi.org/10.1016/j.matpr.2020.04.657

Siwińska-Stefańska, K., Kubiak, A., Piasecki, A., Dobrowolska, A., Czaczyk, K., Motylenko, M., Rafaja, D., Ehrlich, H., Jesionowski, T., 2019. Hydrothermal synthesis of multifunctional TiO 2 -ZnO oxide systems with desired antibacterial and photocatalytic properties. Appl. Surf. Sci. 463, 791–801. https://doi.org/10.1016/j.apsusc.2018.08.256

Siwińska-Stefańska, K., Kubiak, A., Piasecki, A., Goscianska, J., Nowaczyk, G., Jurga, S., Jesionowski, T., 2018. TiO2-ZnO binary oxide systems: Comprehensive characterization and tests of photocatalytic activity. Materials (Basel). 11, 1–19. https://doi.org/10.3390/ma11050841

Skompska, M., Zarebska, K., 2014. Electrodeposition of ZnO Nanorod Arrays on Transparent Conducting Substrates–a Review. Electrochim. Acta 127, 467–488.

https://doi.org/10.1016/j.electacta.2014.02.049

Soares, L., Alves, A., 2018. Photocatalytic properties of TiO 2 and TiO 2 / WO 3 films applied as semiconductors in heterogeneous photocatalysis 211, 339–342. https://doi.org/10.1016/j.matlet.2017.10.023

Song, L., Jiang, Q., Du, P., Yang, Y., Xiong, J., Cui, C., 2014. Novel structure of TiO2-ZnO core shell rice grain for photoanode of dye-sensitized solar cells. J. Power Sources 261, 1–6. https://doi.org/10.1016/j.jpowsour.2014.03.030

Su, Z., Zhang, L., Prof, F., Hong, M., 2013. Formation of crystalline TiO2 by anodic oxidation of titanium. Prog. Nat. Sci. Mater. Int. 23, 294–301. https://doi.org/10.1016/j.pnsc.2013.04.004

Sun, S., Jiao, S., Zhang, K., Wang, D., Gao, S., Li, H., Wang, J., Yu, Q., Guo, F., Zhao, L., 2012. Nucleation effect and growth mechanism of ZnO nanostructures by electrodeposition from aqueous zinc nitrate baths. J. Cryst. Growth 359, 15–19. https://doi.org/10.1016/j.jcrysgro.2012.08.016

Sun, W., Cui, S., Wei, N., Chen, S., Liu, Y., Wang, D., 2018. Hierarchical WO3/TiO2 nanotube nanocomposites for efficient photocathodic protection of 304 stainless steel under visible light. J. Alloys Compd. 749, 741–749. https://doi.org/10.1016/j.jallcom.2018.03.371

Tan, A.W., Pingguan-Murphy, B., Ahmad, R., Akbar, S.A., 2012. Review of titania nanotubes: Fabrication and cellular response. Ceram. Int. 38, 4421–4435. https://doi.org/https://doi.org/10.1016/j.ceramint.2012.03.002

Tian, J., Zhao, Z., Kumar, A., Boughton, R.I., Liu, H., 2014. Recent progress in design, synthesis, and applications of one-dimensional TiO2 nanostructured surface heterostructures: A review. Chem. Soc. Rev. 43, 6920–6937.

https://doi.org/10.1039/c4cs00180j

Tian, Z.R., Voigt, J.A., Liu, J., McKenzie, B., Xu, H., 2003. Large oriented arrays and continuous films of TiO2-based nanotubes. J. Am. Chem. Soc. 125, 12384–12385. https://doi.org/10.1021/ja0369461

Tobajas, M., Belver, C., Rodriguez, J.J., 2017. Degradation of emerging pollutants in water under solar irradiation using novel TiO 2 -ZnO / clay nanoarchitectures. Chem. Eng. J. 309, 596–606. https://doi.org/10.1016/j.cej.2016.10.002

Topo, A., 2013. Wet Production Methods 1. Interface Science and Technology. https://doi.org/10.1016/B978-0-12-369550-5.00002-1

Tsui, L.K., Homma, T., Zangari, G., 2013. Photocurrent conversion in anodized TiO2 nanotube arrays: Effect of the water content in anodizing solutions. J. Phys. Chem. C 117, 6979–6989. https://doi.org/10.1021/jp400318n

Tsuji, E., Taguchi, Y., Aoki, Y., Hashimoto, T., Skeldon, P., Thompson, G., Habazaki, H., 2014. Morphological control of anodic crystalline TiO2 nanochannel films for use in size-selective photocatalytic decomposition of organic molecules. Appl. Surf. Sci. 301. https://doi.org/10.1016/j.apsusc.2014.02.113

Tsvetkov, N., Larina, L., Kang, J.K., Shevaleevskiy, O., 2020. Sol-gel processed tio2 nanotube photoelectrodes for dye-sensitized solar cells with enhanced photovoltaic performance. Nanomaterials 10. https://doi.org/10.3390/nano10020296

Valden, M., Lai, X., Goodman, D.W., 1998. Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. Science (80-.). 281, 1647–1650. https://doi.org/10.1126/science.281.5383.1647

Velempini, T., Prabakaran, E., Pillay, K., 2021. Recent developments in the use of metal oxides for photocatalytic degradation of pharmaceutical pollutants in

water—a review. Mater. Today Chem. 19, 100380. https://doi.org/10.1016/j.mtchem.2020.100380

Waghmode, B., Husain, Z., Joshi, M., Sathaye, S., Patil, K., Malkhede, D., 2016. Synthesis and study of calixarene-doped polypyrrole-TiO2/ZnO composites: Antimicrobial activity and electrochemical sensors. J. Polym. Res. 23. https://doi.org/10.1007/s10965-016-0921-9

Wang, D., Liu, Y., Yu, B., Zhou, F., Liu, W., 2009. TiO2 nanotubes with tunable morphology, diameter, and length: Synthesis and photo-electrical/catalytic performance. Chem. Mater. 21, 1198–1206. https://doi.org/10.1021/cm802384y

Wang, D., Zhang, X., Sun, P., Lu, S., Wang, L., Wang, C., Liu, Y., 2014. Photoelectrochemical water splitting with rutile TiO2 nanowires array: Synergistic effect of hydrogen treatment and surface modification with anatase nanoparticles. Electrochim. Acta 130, 290–295. https://doi.org/10.1016/j.electacta.2014.03.024

Wang, H., Guo, Z., Wang, S., Liu, W., 2014. One-dimensional titania nanostructures: Synthesis and applications in dye-sensitized solar cells. Thin Solid Films 558, 1–19. https://doi.org/10.1016/j.tsf.2014.01.056

Wang, M., Ioccozia, J., Sun, L., Lin, C., Lin, Z., 2014. Inorganic-modified semiconductor TiO2 nanotube arrays for photocatalysis. Energy Environ. Sci. 7, 2182–2202. https://doi.org/10.1039/c4ee00147h

Wang, M., Sun, L., Cai, J., Huang, P., Su, Y., Lin, C., 2013. A facile hydrothermal deposition of ZnFe2O4 nanoparticles on TiO2 nanotube arrays for enhanced visible light photocatalytic activity. J. Mater. Chem. A 1. https://doi.org/10.1039/C3TA12577G

Wang, X., Li, W., Xiao, Y., Zhu, L., Liu, X., 2013. ZnO-TiO_2 Composite Material

Prepared by Sol-Gel Method to Treat Pharmaceutical Wastewater. Appl. Mech. Mater. 361–363, 736–739. https://doi.org/10.4028/www.scientific.net/AMM.361-363.736

Wang, X., Li, Z., Shi, J., Yu, Y., 2014. One-dimensional titanium dioxide nanomaterials: Nanowires, nanorods, and nanobelts. Chem. Rev. 114, 9346–9384. https://doi.org/10.1021/cr400633s

Xia, B.Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., Gates, B., Yin, Y., Kim, F., Yan, H., 2003. One-Dimensional Nanostructures : Synthesis , Characterization , and Applications ** 353–389.

Xie, Y.L., Li, Z.X., Xu, Z.G., Zhang, H.L., 2011. Preparation of coaxial TiO2/ZnO nanotube arrays for high-efficiency photo-energy conversion applications. Electrochem. commun. 13, 788–791. https://doi.org/10.1016/j.elecom.2011.05.003

Xiong Zhang, Guanghui Chen, W.L. and D.W., 2019. Preparation and Photocathodic Protection Properties. Materials (Basel). 12, 3856.

Xu, F., Lu, Y., Xie, Y., Liu, Y., 2009. Controllable morphology evolution of electrodeposited ZnO nano / micro-scale structures in aqueous solution. Mater. Des. 30, 1704–1711. https://doi.org/10.1016/j.matdes.2008.07.024

Xu, F., Mei, J., Li, X., Sun, Y., Wu, D., Gao, Z., Zhang, Q., Jiang, K., 2017. Heterogeneous three-dimensional TiO2/ZnO nanorod array for enhanced photoelectrochemical water splitting properties. J. Nanoparticle Res. 19. https://doi.org/10.1007/s11051-017-3982-8

Xu, L., Liao, Q., Zhang, J., Ai, X., Xu, D., 2007. Single-Crystalline ZnO Nanotube Arrays on Conductive Glass Substrates by Selective Disolution of Electrodeposited ZnO Nanorods 4549–4552.

Xu, X., Wang, J., Tian, J., Wang, X., Dai, J., Liu, X., 2011. Hydrothermal and post-heat treatments of TiO2/ZnO composite powder and its photodegradation behavior on methyl orange. Ceram. Int. 37, 2201–2206. https://doi.org/10.1016/j.ceramint.2011.03.067

Xue, B., Liang, Y., Donglai, L., Eryong, N., Congli, S., Huanhuan, F., Jingjing, X., Yong, J., Zhifeng, J., Xiaosong, S., 2011. Electrodeposition from ZnO nano-rods to nano-sheets with only zinc nitrate electrolyte and its photoluminescence. Appl. Surf. Sci. 257, 10317–10321. https://doi.org/10.1016/j.apsusc.2011.05.132

Yamabi, S., Imai, H., 2002. Growth conditions for wurtzite zinc oxide films in aqueous solutions. J. Mater. Chem. 12, 3773–3778. https://doi.org/10.1039/b205384e

Yang, H.Y., Yu, S.F., Lau, S.P., Zhang, X., Sun, D.D., Jun, G., 2009. Direct Growth of ZnO Nanocrystals onto the Surface of Porous TiO 2 Nanotube Arrays for Highly Efficient and Recyclable Photocatalysts. Small 5, 2260–2264. https://doi.org/10.1002/smll.200900724

Yang, J., Ma, D., Li, Y., Zhang, P., Mi, H., Deng, L., Sun, L., Ren, X., 2017a. Atomic layer deposition of amorphous oxygen-deficient TiO2-x on carbon nanotubes as cathode materials for lithium-air batteries. J. Power Sources 360, 215–220. https://doi.org/10.1016/j.jpowsour.2017.05.094

Yang, J., Mi, H., Luo, S., Li, Y., Zhang, P., Deng, L., Sun, L., Ren, X., 2017b. Atomic layer deposition of TiO2 on nitrogen-doped carbon nanofibers supported Ru nanoparticles for flexible Li-O2 battery: A combined DFT and experimental study. J. Power Sources 368, 88–96. https://doi.org/10.1016/j.jpowsour.2017.09.073

Yang, M., Shrestha, N.K., Schmuki, P., 2009. Thick porous tungsten trioxide films by anodization of tungsten in fluoride containing phosphoric acid electrolyte.

Electrochem. commun. 11, 1908–1911. https://doi.org/10.1016/j.elecom.2009.08.014

Yao, B.D., Chan, Y.F., Zhang, X.Y., Zhang, W.F., Yang, Z.Y., Wang, N., 2003. Formation mechanism of TiO2 nanotubes. Appl. Phys. Lett. 82, 281–283. https://doi.org/10.1063/1.1537518

Yilmaz, C., Unal, U., 2016. Effect of Zn(NO 3)2 concentration in hydrothermal-electrochemical deposition on morphology and photoelectrochemical properties of ZnO nanorods. Appl. Surf. Sci. 368, 456–463. https://doi.org/10.1016/j.apsusc.2016.01.253

Yoon, S., Kim, J., Yoo, B., Lim, J.-H., 2016. Electrochemical Synthesis of Nanostructured Materials for Solar Energy Conversion. https://doi.org/10.1364/PV.2016.PTh4A.1

Yoshida, T., Komatsu, D., Shimokawa, N., Minoura, H., 2004. Mechanism of cathodic electrodeposition of zinc oxide thin films from aqueous zinc nitrate baths. Thin Solid Films 451–452, 166–169. https://doi.org/10.1016/j.tsf.2003.10.097

Yu, J., Wang, B., 2010. Effect of calcination temperature on morphology and photoelectrochemical properties of anodized titanium dioxide nanotube arrays. Appl. Catal. B Environ. 94, 295–302. https://doi.org/10.1016/j.apcatb.2009.12.003

Yu, X., Lin, D., Li, P., Su, Z., 2017. Recent advances in the synthesis and energy applications of TiO2-graphene nanohybrids. Sol. Energy Mater. Sol. Cells 172, 252–269. https://doi.org/10.1016/j.solmat.2017.07.045

Yuan, S., Chen, C., Raza, A., Song, R., Zhang, T.J., Pehkonen, S.O., Liang, B., 2017. Nanostructured TiO2/CuO dual-coated copper meshes with superhydrophilic, underwater superoleophobic and self-cleaning properties for highly efficient

oil/water separation. Chem. Eng. J. 328, 497–510. https://doi.org/10.1016/j.cej.2017.07.075

Zaitsev, S. V., Vaschilin, V.S., Kolesnik, V. V., Limarenko, M. V., Prokhorenkov, D.S., Evtushenko, E.I., 2019. Effect of the Temperature of Photonic Annealing on the Structural and Optical Properties of ZnO Films Synthesized by Dual Magnetron-Assisted Sputtering. Semiconductors 53, 255–259. https://doi.org/10.1134/S106378261902026X

Zangari, G., 2018. Fundamentals of electrodeposition. Encycl. Interfacial Chem. Surf. Sci. Electrochem. 141–160. https://doi.org/10.1016/B978-0-12-409547-2.11700-7

Zhang, D., Gu, X., Jing, F., Gao, F., Zhou, J., Ruan, S., 2015. High performance ultraviolet detector based on TiO2/ZnO heterojunction. J. Alloys Compd. 618, 551–554. https://doi.org/https://doi.org/10.1016/j.jallcom.2014.09.004

Zhang, Q., Cao, G., 2011. Nanostructured photoelectrodes for dye-sensitized solar cells. Nano Today 6, 91–109. https://doi.org/10.1016/j.nantod.2010.12.007

Zhang, R., Liu, X., Xiong, Z., Huang, Q., Yang, X., Yan, H., Ma, J., Feng, Q., Shen, Z., 2018. Novel micro/nanostructured TiO2/ZnO coating with antibacterial capacity and cytocompatibility. Ceram. Int. 44, 9711–9719. https://doi.org/https://doi.org/10.1016/j.ceramint.2018.02.202

Zhang, Y.X., Li, G.H., Jin, Y.X., Zhang, Y., Zhang, J., Zhang, L.D., 2002. Hydrothermal synthesis and photoluminescence of TiO2 nanowires. Chem. Phys. Lett. 365, 300–304. https://doi.org/10.1016/S0009-2614(02)01499-9

Zhang, Z., Xu, P., Zhang, H., Shen, A., Zhao, Y., 2019. Flexible Three-Dimensional Titanium-Dioxide-Based Hollow Nanoflower Arrays for Advanced Lithium-Ion Battery Anodes. ACS Appl. Energy Mater. 2, 5744–5752.

https://doi.org/10.1021/acsaem.9b00869

Zhang, Z., Yuan, Y., Liang, L., Cheng, Y., Shi, G., Jin, L., 2008. Preparation and photoelectrocatalytic activity of ZnO nanorods embedded in highly ordered TiO2 nanotube arrays electrode for azo dye degradation. J. Hazard. Mater. 158, 517–522. https://doi.org/10.1016/j.jhazmat.2008.01.118

Zhou, M., Wu, B., Zhang, X., Cao, S., Ma, P., Wang, K., Fan, Z., Su, M., 2020. Preparation and UV Photoelectric Properties of Aligned ZnO–TiO2 and TiO2–ZnO Core–Shell Structured Heterojunction Nanotubes. ACS Appl. Mater. Interfaces 12, 38490–38498. https://doi.org/10.1021/acsami.0c03550

Zhou, W., Liu, H., Boughton, R.I., Du, G., Lin, J., Wang, J., Liu, D., 2010. One-dimensional single-crystalline Ti-O based nanostructures: Properties, synthesis, modifications and applications. J. Mater. Chem. 20, 5993–6008. https://doi.org/10.1039/b927224k

Zhou, X., Nguyen, N.T., Özkan, S., Schmuki, P., 2014. Anodic TiO2 nanotube layers: Why does self-organized growth occur-A mini review. Electrochem. commun. 46. https://doi.org/10.1016/j.elecom.2014.06.021

Zhu, H., Haidry, A.A., Wang, Z., Ji, Y., 2021. Improved acetone sensing characteristics of TiO2 nanobelts with Ag modification. J. Alloys Compd. 887, 161312. https://doi.org/10.1016/j.jallcom.2021.161312

Znaidi, L., 2010. Sol-gel-deposited ZnO thin films: A review. Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 174, 18–30. https://doi.org/10.1016/j.mseb.2010.07.001

Zwilling, V., Darque-Ceretti, E., Boutry-Forveille, A., David, D., Perrin, M.Y., Aucouturier, M., 1999. Structure and Physicochemistry of Anodic Oxide Films on

Titanium and TA6V Alloy. Surf. Interface Anal. https://doi.org/10.1002/(SICI)1096-9918(199907)27:7<629::AID-SIA551>3.0.CO;2-0

Figure captions

Figure 1. FESEM images of TiO_2 a) nanowires (Zhang et al., 2002), b) nanobelts (Zhu et al., 2021), c) nanorods (Lv et al., 2018) and d) nanotubes (Sivaprakash and Narayanan, 2020).

Figure 2. Stages of the electrochemical anodization process of Ti using electrolytes with fluorides (Sánchez-Tovar et al., 2020).

Figure 3. Regions of existence of TiO_2 nanotubes, nanosponges and compact layers, as a function of [NH_4F], revolutions per minute (RPM) of the working electrode and the potential (Sánchez-Tovar et al., 2013).

Figure 4. FESEM images and GAXRD patterns of TiO_2 of TiO_2 nanotubes synthesised by electrochemical anodization a room temperature (Allam and Grimes, 2009).

Figure 5. Photoluminescence of TiO_2 nanostructures as a function of annealing temperature (Yu and Wang, 2010).

Figure 6. Schematic diagram of the energy level for heterojunction of TiO_2/ZnO hybrid nanostructures.

Figure 7. Coverage ratio and diameter as a function of $Zn(NO_3)_2$ concentration (Sun et al., 2012).

Figure 8. Comparison of phase stability diagrams of a) ZnO(s) and b) $Zn(OH)_2$(s) in aqueous solutions at 25 °C (Yamabi and Imai, 2002).

Figure 9. a) Photocurrent density-voltage curves and b) IPCE spectra for TiO_2 nanotubes and coaxial TiO_2/ZnO nanotubes (Xie et al., 2011).

Figure 10. Photodegradation curves of P-Cresol (100 ppm) under UV illumination using: a control experiment without photocatalyst (●), ZnO (□), TiO_2 (△), TiO_2/ZnO (▲) and TiO_2/ZnO/PANI (+) (Brooms et al., 2017).

Figure 11. a) Photodegradation curves of 2,4-DNP using a) TiO_2, ZnO and TiO_2/ZnO hollow microspheres and b) TiO_2/ZnO hollow microspheres and Commercial P25 (TiO_2 nanoparticles) (Liu et al., 2017).

Figure 12. Scheme of the photoelectrochemical water splitting.

Figure 13. Schematic diagram of a) structure and b) energy level for heterojunction of TiO_2/ZnO (Feng et al., 2017).

Figure 14. a) Photocurrent density vs potential under UV (100 mW/cm^2) illumination, b) photoconversion efficiency and c) IPCE under a constant bias of 0.6 V for pure TiO_2 nanotubes and TiO_2/ZnO nanotubes sputtered for 53 min (Shaheen et al., 2013).

Figure 15. a) Wavelength and spectral response as a function of the concentration of hydrogen sulfide and b) dynamic response for the TiO_2/ZnO sensors (Feng et al., 2021).

Figure 16. a) Charge-discharge voltage profiles of TiO_2/ZnO hollow nanoflower arrays at a constant current rate of 200 $mA \cdot g^{-1}$ and b) cycling performances of TiO_2/ZnO hollow nanoflower arrays, TiO_2 hollow nanofiber arrays and ZnO nanorod arrays (Zhang et al., 2019).

Table captions

Table 1. Examples of procedures to form TiO_2 nanotubes by electrochemical anodization of Ti.

Table 2. Examples of procedures to electrodeposit ZnO on TiO_2 nanostructures.

Table 3. Comparison of adsorption capacity of TiO_2/ZnO nanofibers with other nanofibers adsorbents for Cu(II) and Ni(II) sorption for Cu(II) and Ni(II) sorption (Khosravi et al., 2020).