REVIEW

Visible light responsive titania-based nanostructures for photocatalytic, photovoltaic and photoelectrochemical applications

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Abstract
This work presents a topical review of selected articles on visible light responsive titania-based nanostructures used for fabricating the photoanodes of the photocatalytic and photoelectrical cells for hydrogen production by water splitting or fuel decomposition, electricity generation by fuel decomposition and pollutant degradation under illumination by sunlight as well as for fabricating dye-sensitized and quantum dot-sensitized solar cells. Three main types of related nanostructures are reviewed: anion-doped titania nanomaterials, cation-doped titania nanomaterials and titania-based nanostructures sensitized by dyes and quantum dots. After the presentation of the obtained results, the prospective further research works to achieve the successful fabrication of visible light responsive photocatalytic, photoelectrochemical or photovoltaic devices with high performance are discussed.

Keywords: solar cell, doping, nanostructure, nanomaterial

Classification numbers: 4.01, 4.02, 5.04, 5.07

1. Introduction

The celebrated experiment of Fujishima and Honda [1] on pure water splitting in a photoelectrochemical (PEC) cell using a titania photoanode has inspired widespread interest from the scientific community in the study of solar energy conversion into hydrogen energy and/or electricity. A very large number of semiconductor materials which can be used for fabricating the photoanodes of PEC cells have been prepared, characterized and used in experimental studies on solar energy conversion. Many comprehensive reviews on semiconductor photocatalytic (PC) materials have been published (see, for example, [2, 3]). Among all PC materials, titania is the most prospective [4, 5], because it is chemically inert, non-toxic, photostable and has low cost. However, titania has one disadvantage: due to its large bandgap (3.2 eV for anatase) it is not sensible with respect to visible light. To overcome this disadvantage many experiments have been done in which the electronic structure of titania has been modified by doping for preparing visible light responsive PC materials, or titania nanomaterial has been sensitized for fabricating visible light responsive photoanodes of PEC cells. The present article is a comparative review of selected typical related works with discussions on the basic physical characteristics of prepared nanomaterials, such as the edges of electron energy bands, the presence of deep energy levels in the bandgap and the evidence of the separation of the excited charge carriers.

The PC activities of the prepared nanomaterials as well as the working abilities of PEC cells are determined by several factors: the sensibility of the visible light absorption, the separation of the exited charge carriers to prevent
electron-hole recombination and/or the electron relaxation due to the presence of defects and impurities, including doping elements, the Brunauer-Emmett-Teller (BET) surface areas of the PC materials, the catalytic reactions at the surfaces of the PC materials or at the surface of the counter cathodes of PEC cells, the chemical reactions in the electrolytes etc. The comprehensive study of the above-mentioned characteristics of each type of PC material or PEC photoanode (as well as the chemical reactions in the electrolyte, if it is necessary) would give the complete scientific data for the design of the most effective PC material or PEC photoanode of the corresponding type. It was well-known that one of the effective methods to observe the deep impurity centers in the bandgap of a semiconductor is the investigation of the photoluminescence spectrum. Moreover, the charge separation in the semiconductor nanostructure would decrease its luminescence intensity. Therefore the observed decrease of the luminescence intensity would be the evidence of the charge separation. Promoting research on this topic is one of the aims of the present article.

The review of typical works on anion-doped titania nanomaterials is presented in section 2. Results of different works and conclusions of their authors are compared and discussed. Section 3 is devoted to the review of the typical works on cation-doped titania nanomaterials. In section 4 we review the main results of study on dye-sensitized solar cells (DSSCs) and similar PEC cells with fuels as organic sacrified agents for generating electricity—the photofuel cells (PFCs). It was proposed to replace the dyes in DSSCs by quantum dots (QDs). The main results of the study of QD-sensitized solar cells (QDSSCs) are also reviewed in section 4. The conclusion and discussions on the prospective studies of the reviewed issues are presented in section 5.

2. Anion-doped titania nanomaterials

The earliest experimental work to chemically modify titania for preparing a visible-light responsive photocatalyst has been performed by Fujishima et al [6]. Although these authors did not investigate the absorption spectrum of the modified titania, the ability of the modified photocatalyst to split water under the illumination by sunlight, which contains only a very small fraction of UV light, might signify that the energy bandgap was narrowed. Different methods to modify the structure of titania for preparing photocatalysts with bandgaps narrower than that of pure titania have been discussed by Asahi et al [7]. They noticed that reducing titania creates localized oxygen vacancy states in the interval 0.75–1.18 eV below the titania conduction band minimum (CBM), so that the energy levels of optically excited electrons are lower than the redox potential of the hydrogen evolution (H$_2$/H$_2$O) located just below the titania CBM. Moreover, due to the localization the electrons have a small mobility. Concerning the doped titania, the following conditions are required:

(i) Doped titania should have a narrow energy band gap to absorb visible light.
(ii) CBM of doped titania should be as high as that of pure titania or higher than the H$_2$/H$_2$O redox potential to ensure the photoreduction.
(iii) Wave functions of the states in the bandgap should overlap sufficiently with those of the band states of titania to transfer photoexcited electron to the reactive sites at the surface of the photocatalyst.

Because the doping by transition metals (cation-doping) often creates localized d states with deep energy levels in the energy bandgap which violate conditions (ii) and (iii) and results in the appearance of the recombination centers of the carriers, Asahi et al [7] prefer doping by non-metallic elements C, N, F, P or S (anion-doping). They have done full-potential linearized augmented plane wave (FLAPW) calculation and shown that substitutional doping by N is the most effective. Its p states cause the bandgap narrowing by mixing with O 2p states. The N-doped titania nanocrystalline films (NCFs) were prepared by sputtering the titania target in an N(40%)Ar gas mixture. Photocatalytic activity was evaluated by measuring decomposition rate of methylene blue under the visible light. The active wavelength range of N-doped titania covers the main peak of the solar light spectrum.

Asahi et al [7] measured the absorption spectra of both pure and N-doped titania NCFs. Although they observed the redshift of the absorption spectrum of N-doped titania up to the wavelength of 500 nm, they could not determine the value of the narrowed bandgap. With the resolution of the absorption spectrum of N-doped titania nanomaterials until now one could not also find discrete energy levels inside the bandgap if they do exist. The absorption spectra should be measured with better resolutions. The results of subsequent experimental works [8–11] agreed well with the conclusion of Asahi et al [7] concerning N-doped titania.

In a series of interesting experimental works by Anpo et al [12–20] the doping of nitrogen to titania was also performed by the radiofrequency magnetron sputtering (RF-MS) technique to prepare visible-light responsive PC thin films denoted Vis-TiO$_2$. The source material to be sputtered was that in a titania target and the sputtering gas was a mixture of N and Ar gases. As a result of the bombardment by a large number of high energy sputtered atoms, the O/TiO$_2$ composition in the prepared substrate from the surface to deep inside the film became different from that of the initial substrate. It was shown that for the splitting of pure water into hydrogen under illumination by visible or solar light the prepared modified titania film has rather high reactivity. This PC property might be a consequence of the narrowing of the energy bandgap due to the nitrogen doping. It would be worth carrying out spectroscopic investigations of this type of modified titania to reveal its electronic structure, in particular to determine its energy bandgap and also to observe the deep levels inside the energy bandgap due to the defects or the impurity centers.

In spite of the arguments of Asahi et al [7] in favor of N-doping to titania, Khan et al [21] investigated C-doped titania film prepared by flame pyrolysis of Ti metal sheet in the presence of combustion products (CO$_2$ and H$_2$O steam) in a natural gas flame. This preparation method was similar to that used in reference [6]. The x-ray photoelectron spectroscopy (XPS) data of the samples prepared in [21] showed that they did not contain nitrogen. From the UV–visible absorption spectra of these samples the authors have derived the values 535 and 440 nm of two optical absorption thresholds.
corresponding to two bandgap energies 2.32 and 2.82 eV. They have also measured the maximum photoconversion efficiency under illumination by a 150 W xenon lamp and obtained a value eight times larger than that of the pure titania. Subsequently Khan and co-workers [22–25] continued to prepare C-doped titania nanoparticles by means of different methods and to study the physical characteristic as well as the photocatalytic activities of the prepared samples. In [22] the authors synthesized C-doped titania nanoparticles by wet chemical process using glucose solution as the carbon source and reported the extension of the absorption spectrum of prepared samples up to the wavelength of 800 nm as well as the thirteen fold increase of the catalytic activity in comparison with that of pure titania. By a treatment of the UV–visible absorption spectrum they have shown that the energy bandgap lowered from 3.20 to 2.78 eV. Moreover, there appeared a mid-gap band at 1.45 eV. In [25] a comprehensive study of visible light active C-doped titania for efficient hydrogen production by PEC splitting of water has been done. The samples were prepared by thermally oxidizing Ti metal sheets in the flame under the controlled natural gas and oxygen flows. The PEC activities of the material were investigated under the illumination by a 150 W xenon lamp and the applied potential of 0.24 V. By means of a careful treatment of the absorption spectrum the authors have shown the existence of two energy bandgaps: the first bandgap of 2.7 eV resulted by reducing the original energy bandgap of 3 eV for rutile titania and the mid-band gap of 1.6 eV caused by C-doping. The treatment method of these authors should be applied in all future works on a similar subject. It would also be worth measuring the photoluminescence spectra of the samples in addition to the absorption ones.

From the results of the experimental works of Khan et al [21–25] it can be concluded that the physical characteristics and PEC activities of C-doped titania nanoparticles depend on the methods which were used for preparing the samples, and C-doped titania is also a promising visible light active photocatalytic material. The last conclusion agreed well with the result of [26] in which the authors have observed a five fold increase in photocatalytic activity of C-doped titania compared to N-doped. This interesting experiment of Khan et al [21] inspired many authors to continue to study C-doped titania nanocrystalline films [27–34]. Their results agreed well with the conclusions of the recent work of Shahan and Khan et al [25].

Besides the wide interest in studying the PC properties of nanoparticles (NPs) and nanocrystalline films (NCFs) of N-doped [6–20, 35–40] and C-doped [21–34, 41–45] titania, those of S-doped [46–51], F-doped [52–55], P-doped [56–59] and N/P-co-doped [60–62], N/C-co-doped [63, 64], N/S-co-doped [65] titania were also prepared and their PC properties were investigated. Recently, owing to the progress of nanotechnology, C-doped titania nanotube as well as nanotube array [66, 67] and N-doped titania nanotube [68] were fabricated. They have superior PC activities in comparison with NPs and NCFs of C-doped and N-doped titania, respectively.

In concluding this section we note that, except for a few above-presented typical works, in most experimental studies on anion-doped titania nanomaterials the main attention was paid to the determination of overall PC properties of the fabricated samples. This is necessary for evaluating the feasible utilization of prepared nanomaterials in practice. However, in order to find the way to improve the PC properties of these nanomaterials, their electronic energy band structures, including the presence of the discrete deep levels in the energy bandgaps, as well as the dynamical phenomena and processes determining their PC activities should be investigated in detail. This issue will be discussed again in the last section of this review.

3. Cation-doped titania nanomaterials

The attempts to prepare visible light responsive cation-doped titania nanoparticles (NPs) and nanocrystalline films (NCFs) also arose a long time ago [69–71]. At the beginning the dopants were transition metal elements. Subsequently some rare earth elements were also used as the dopants. The three most attractive transition metal elements for using as dopants were Cu, Fe and Pt.

Copper may be present in the visible light responsive titania-based nanostructures either as a dopant in the titania nanocrystal or as the metallic element in the semiconductor compounds CuO and Cu2O to be used as visible light sensitizers of titania nanocrystal. In recent years there arose a strong interest in the research on Cu-doped titania as a visible light responsive photocatalyst [72–76]. In a recent work Sun and co-authors [76] have obtained valuable results. These authors prepared Cu-doped titania samples by four different methods, namely, in situ sol–gel (SG), wet impregnation (WI), chemical reduction of Cu salt by NaBH4 (NR) and in situ photodeposition (PD). SG sample possessed the largest BET surface area of 87.3 m2 g–1, while WI, NR and PD samples have moderate ones of 36.1, 44.8 and 46.8 m2 g–1, respectively. The PC hydrogen generation over the samples of all four types was investigated. The UV–visible absorption spectra of all samples were measured. These spectra have large absorption bands between wavelength values 400 and 800 nm. However, from these spectra the edges of the energy bandgaps that are narrower than those of pure titania cannot be determined and the discrete deep levels inside the energy bandgap of pure titania were not seen.

Titania NCFs and NPs were also doped by Fe3+ ions [77–81]. With Fe3+ ion concentration lower than 0.03 mol%, Fe-doped titania is a visible light responsive photocatalyst. However, at Fe3+ ion concentration exceeding 0.03 mol%, oxide molecules Fe3O4 would be formed and become the recombination centers of photoexcited charge carriers, which would prevent the separation of free electrons and holes generated by the light absorption of the photocatalyst.

Since the early days of photocatalysis study it was know that, as a co-catalyst, noble metal Pt deposited on the surfaces of titania NPs or NCFs would significantly improve their PC activity. In the role of a scavenger of electrons Pt NPs deposited on these surfaces would trap the electrons of the photogenerated electron-hole pairs inside the PC nanomaterials and therefore would stimulate the charge separation and prevent the recombination of the excited electrons. These trapped electrons would then rapidly
transfer from the surfaces of the nanomaterials to the surrounding media (electrolyte, for example) and therefore, the catalytic reactions at these surfaces would be enhanced. Beside the above-mentioned double role of a co-catalyst and, at the same time, of a scavenger of electrons, Pt can play one more role—that of a cation dopant in the titania nanocrystal [82–84]. A series of experimental works on Pt-doped titania nanomaterials have been done by Yang and co-workers [85–88]. Very interesting results were obtained in [88]. In this last work the authors synthesized titania nanotube (TiNT) by hydrothermal method and introduced Pt onto TiNT by means of the ion exchange method. The prepared material was denoted Pt(IE)/TiNT. For comparison Pt was also introduced onto TiNT by means of the impregnation method and the prepared material was denoted Pt(Imp)/TiNT. The samples of TiNT, Pt(Imp)/TiNT and Pt(IE)/TiNT have BET surface areas of 98.8 and 92 m² g⁻¹, respectively, while that of the starting material TiO₂(P-25) is 50 m² g⁻¹. This result demonstrated the privilege of one-dimensional titania nanostructures in comparison with particulate ones. While TiNT and Pt(Imp)/TiNT have the same bandgap energy of 3.1 eV as that of TiO₂(P-25), Pt(IE)/TiNT has a lower bandgap energy of 2.48 eV. These values of the bandgap energies were derived on the basis of treatment of the UV–visible diffuse reflectance spectroscopy (DRS) spectra of the samples. It would be worth measuring their absorption and luminescence spectra. With a good resolution they would also give information on the discrete energy deep levels inside the bandgap. The study of the H₂ and O₂ evolution from the spitting of water and the measurement of photoresponse confirmed the much higher PC activity of Pt(IE)/TiNT under sunlight in comparison with that of Pt(Imp)/TiNT.

Besides Pt as the most typical co-catalyst, two other noble metals Au and Ag in the form of NPs were also deposited on the surface of photocatalyst for enhancing catalytic reactions at these surfaces as the co-catalysts. Moreover, in [89, 90] Au and Au⁺ were doped to titania nanocrystals to transform them into visible light responsive nanomaterials. In [91] it was shown that Ag-doped titania is also a visible light responsive photocatalyst.

Besides the above-mentioned cation dopants, many other transition metals were used for doping titania nanomaterials to prepare visible light responsive nanophotocatalysts. Among them, vanadium is a promising element [92, 93]. In [93] not only V, but other transition metals W, Zr, Cu and Fe were also doped to titania. Cr⁺⁺⁺-doped titania nanomaterials were prepared in [80, 94], and Co⁺⁺⁺-doped ones in [80]. Visible light responsive titania-based cation-doped nanomaterials of very high quality were fabricated by means of the ion implantation technique in celebrated experiments of Anpo et al [95–97]. Although this method is expensive and could not be used for widespread applications in practice, it is extremely useful for the fundamental experimental studies on the electronic structures of the related nanophotocatalysts as well as on the principal physical and chemical phenomena and processes in these nanomaterials. Modification of titania nanomaterials by doping transition metals to them was also performed in recent works [98–104]. Titania-based nanomaterials co-doped by two transition metals Cr and Sb were prepared and investigated in [105–107]. Co-doping a titania nanomaterial by cation Bi and anion S was also done in [108].

Not only were transition metals doped to titania nanomaterials for transforming them into visible light responsive nanophotocatalysts, but rare earth elements were also used as the cation dopant. For example, in addition to the use of different transition metals, Nagaveni et al [93] prepared and investigated Ce-doped titania nanomaterial. In a series of experiments of Xie et al [109–112], modified titania nanomaterials were prepared by doping rare earth ions Nd³⁺, Eu³⁺ and Ce⁴⁺. Er³⁺-doping to titania was done in [113] and Sm-doped titania was prepared in [114].

It is worth noting that in most of the above-mentioned works on visible light responsive cation-doped titania-based nanophotocatalysts their overall PC properties were investigated. Although the photoabsorption spectra of the prepared samples were measured by a few authors, only in very few works was the accuracy of experimental data good enough for the quantitative determination of the shifts of the edges of the photoabsorption spectra. However, the presence of the discrete energy levels inside the bandgap, if they really do exist, was never observed. Finally we remark that the careful analysis of high resolution photoluminescence spectra of prepared cation-doped titania nanomaterials would give useful information on their electronic structures. The photoluminescence spectra of several cation-doped titania nanomaterials were measured in [93]. Experimental works in this direction for all prepared samples and with higher resolutions would be very desirable.

4. Sensitized titania-based nanostructures

For the fabrication of visible light responsive photoanodes of various PEC devices on the basis of titania-based nanostructures, instead of anion- and cation-doping titania nanomaterials there exists another original approach: to sensitize pure titania nanomaterials by attaching to their surfaces different visible light sensitive agents called sensitizers, such as dyes and semiconductor nanocrystals (NCS) playing the role of semiconductor quantum dots (QDs). At the beginning, fabricated visible light responsive nanostructures were used as the photoanodes of corresponding solar cells to generate electricity from solar energy—dye-sensitized solar cells (DSSCs) and quantum dot-sensitized solar cells (QDSSCs). Later on it was proposed to use them as the photoanodes of various PEC devices for green energy technology as well as for depollution. The first experiment on dye-sensitized titania NCF was done in a celebrated work of O’ Regan and Grätzel [115]. Subsequently, Grätzel [116–118] proposed to use them in PEC cells for various other applications. The sensitizer used in [115] was the following dye: trimeric ruthenium complex RuL₂(µ−(CN)Ru(CN)₂)₂, where L is 2, 2′bipyridine-4, 4′-dicarboxylic acid and L’ is 2, 2′bipyridine. In order to sensitize a titania nanocrystalline film with respect to the visible light, a monolayer of the above sensitizer was deposited directly on this film. The absorption spectrum of this sensitized nanostructure is then enlarged up to 750 nm. The significant increase of its absorbance with respect to the
sunlight due to the presence of the sensitizer was clearly seen in the absorption spectrum. This sensitized nanostructure was used for preparing the photoanode of a dye-sensitized solar cell (DSSC). Other sensitizing dyes were used in [116, 117, 119]. The research on DSSCs is still ongoing [119–129].

Nanostructures similar to those in photoanodes of DSSCs were also used for preparing photoanodes of PEC cells for hydrogen generation by splitting pure water or organic fuels as well as for pollutant degradation under illumination by sunlight [117, 118, 130]. The nanostructures used for preparing photoanodes of PEC cells which degrade pollutants under the action of sunlight were also sensitized by other dyes such as thionine, eosin Y, rhodamine B, methylene blue (MB), etc [131–133]. Moreover, the pollutants or fuels to be degraded or consumed (decomposed) during the working process of PEC cells themselves could also play the role of sensitizers: the electron excited from the ground state of a pollutant or a fuel due to the absorption sunlight by this compound is injected into the conduction band of titania nanomaterial and then loaded to the counter cathode. Subsequent reactions in the sacrificed pollutant or fuel lead to its degradation or consumption (decomposition) [134–139]. The presented sensitization ability of pollutants to be degraded or fuels to be consumed (decomposed) opened new perspectives for the utilization of titania-based nanostructures in environmental technology as well as for producing PFCs. In [119–123] the titania nanostructures were sensitized nanotube and nanowire arrays, while in other works the host materials were NCFs.

In order to sensitize titania nanomaterials for fabricating photoanodes of solar cells it was proposed a long time ago to also use QDs [140–145]. The study on QDSSCs is a rather active ongoing research topic at the present time [146–155]. QDSSCs have several advantages in comparison with DSSCs. Because the energy gaps of QDs depend on their sizes, the working wavelengths of QDSSCs are tunable and their range may be wider than those of energy levels of dyes [156]. The photoabsorption coefficients of QDs may be higher than those of dyes (typically by a factor of 5), and QDs have superior resistances against photobleaching over organometallic or organic dyes [157]. CdS is a direct bandgap semiconductor with high photoabsorption coefficient and its QDs in the form of NCs were used as sensitizer by many authors [142, 144, 150, 152, 157–161]. However, it is unstable due to the photocorrosion caused by photogenerated holes

\[ 2h^+ + \text{CdS} \rightarrow \text{Cd}^{2+} + S. \]

CdTe is also photocorroded and less photosensible. For using as sensitizer in QDSSC, the most preferable QD was that of CdSe [147, 155, 162–168]. Sensitizing CdSe QDs were directly deposited onto the surfaces of titania nanomaterials in many experimental works. Attempts were made to connect this type of sensitizing QD with the host nanomaterials through bifunctional linker molecules [162, 167]. The study of the co-sensitization of titania nanomaterials by CdS and CdSe has shown that the performance of CdSe/CdS/TiO\(_2\) nanostructure is higher than that of CdS/TiO\(_2\) and CdSe/TiO\(_2\), but that of CdS/CdSe/TiO\(_2\) nanostructure is lower than the latter [149, 169, 170]. In a recent interesting work [171] CdSe QD was used to sensitize N-doped titania nanomaterial. This new QD-sensitized nanostructure has PEC activity higher than that using a pure titania one.

The efficiencies of QDSSCs are still lower than those of DSSCs, but attempts to improve them are ongoing. For example, the change of the ligand for passivating the surface of QD, namely the replacement of tri-n-octylphosphine oxide (TOPO) by 4-butylamine (BA), a shorter passivating ligand, leads to a significant enhancement of both the electron injection efficiency at the QD/titania NP interface and the charge collection efficiency at the QD/electrolyte interface [153]. The performance of QDSSC can be significantly enhanced by ZnS surface coating [172], SiO\(_2\) surface coating [173], or by introducing a dense TiO\(_2\) blocking layer [174]. Another possibility to enhance the photocurrent in QDSSCs is the exploitation of the carrier multiplication [175, 176], the inverse Auger recombination [166, 177] as well as the multiple exciton photogeneration [178–180]. One more way to improve the performance of QDSSCs is enhancing the photoabsorption of QD sensitized nanomaterials by means of the surface plasmon resonance (SPR) of the metallic nanoparticles directly deposited on their surfaces [181–192]. The physical mechanism of the SPR effect can be briefly described as follows. Surface plasmons (SPs) are the elementary excitations (quasiparticles) of the collective oscillations of itinerant (quasifree) electrons near the surface of the metallic NP. Their resonant coupling with incident photons causes the strong absorption of the incident light, and the metallic NP operates as a nanoantenna for receiving the light [184]. It was known that the resonant frequency is tunable due to its dependence on the size and shape of the metallic NP as well as on the dielectric constant of the surrounding environment [193]. The resonant absorption of the incident light results in the enhancement of the electron-hole pair generation in the best nanostructure. Note that this enhancement physical mechanism is different from the role of co-catalyst played by Au NP in Au/CdS/TiO\(_2\) PC metal-semiconductors nanocomposite [194] or PtNP in Pt/CdS/TiO\(_2\) PC metal-semiconductors nanocomposite [195, 196]. Besides the above-presented sensitization by CdS and CdSe QDs nanocrystals of other semiconductors such as PbS [141, 197], InP [145], InAs [198], CdTe [147, 199], Cu\(_2\)O [200] and CuO [201] can also play the role of sensitizing QDs. A promising sensitizer might be CuSe [202]. Although Si is a semiconductor with indirect bandgap, its photoabsorption coefficient is small, but that of SiQD may become large due to the electron confinement and it is desirable to study the sensitization by using Si nanomaterials. The above-presented QD sensitized titania nanomaterials would be widely used not only in QDSSCs, but also for fabricating photoanodes of various PEC devices (also called cells) for solar energy conversion into hydrogen energy, electricity generation by photoassisted decomposition of fuels (PFC) as well as PC degradation of pollutants under illumination by sunlight [203].

5. Conclusion and discussions

The discovery of the photocatalytic splitting of pure water at the titania electrode by Fujishima and Honda [1] four decades ago has opened a wide and very promising scientific
field—the photocatalytic conversion of solar energy into electricity and hydrogen energy as well as the photocatalytic degradation of pollutants under sunlight illumination. The results of scientific works in this field were published in thousands papers. The present review concerns only a small number of selected works related to visible light responsive titania-based nanomaterials and nanostructures. The results of many other works were included in many published reviews [2–5, 203–210] and monographs [211, 212]. While photoinduced hydrophilicity involving surface self-cleaning and antifogging abilities as well as the PC activity of pure titania under the illumination by UV light were widely applied in practice, many research works should be done until successful and effective practical application of the PC properties of visible light responsive photocatalysts, including titania-based PC nanomaterials and nanostructures, as a promising effective way to exploit the solar energy.

The main contents of this review are presented in three sections. In section 2 the detailed results of typical works on two most promising anion-doped titania nanomaterials, namely N-doped and C-doped ones, were presented. In particular, attention was paid to the careful treatment of the absorption spectrum of C-doped titania nanomaterial which permits clearly determining the values of its energy bandgaps and to reveal a mid-gap band. The latter would signify the existence of a discrete level inside the main energy bandgap [25]. Some other works on anion-doped titania nanomaterials were mentioned. In these last works little or even no attention was paid to the study of the photoabsorption spectra of the prepared samples. No photoluminescence spectrum was measured. In section 3 the detailed results of the typical experimental works on two types of cation-doped titania nanomaterials, namely Cu-doped and Pt-doped ones, were presented. Their photoabsorption spectra as well as their PC properties depend on the preparation methods. Many other experimental studies on different cation-doped titania nanomaterials were briefly reviewed. The photoabsorption spectra of the samples cation-doped by means of the ion implantation techniques [95–97] had good quality permitting clear observation of the shifts of the energy bandgaps due to the doping. The photoabsorption spectra of many other cation-doped titania nanomaterials were also measured but with poor quality. In general the resolution of the observed photoabsorption spectra of all cation-doped titania nanomaterials was not enough to reveal the existence of the discrete levels inside the main energy bandgap. It is interesting to remark that in the photoluminescence spectra of many cation-doped titania nanomaterials, namely W-doped, V-doped, Cu-doped, Fe-doped and Zr-doped ones [93], the new peaks inside the main energy bandgaps were clearly seen. This means that comprehensive experimental studies of the optical processes would provide new important information on the electronic structures of the PC nanomaterials, both cation-doped as well as anion-doped ones. Moreover, the comparative studies of the photoluminescence spectra of the doped titania nanomaterial with and without the Pt co-catalyst deposited on the surface-doped titania NPs or the Pt counter cathode connected with the doped titania photoanode, which play the role of electron scavengers for enhancing the charge separation process, would signify its evident demonstration.

The charge carrier transfer across different interfaces should also be investigated in detail. Recently, the technology of preparing one-dimensional titania nanomaterials, nanotubes, nanowires and nanorods, was elaborated [213–215]. They have surface areas larger than those of titania NPs and NCFs. The replacement of NPs and NCFs by corresponding nanotube or nanorod arrays would significantly improve the PC properties of the photoanodes.

Research on visible light responsive titania-based nanostructures sensitized by dyes and QDs began a long time ago, is still actively ongoing at the present time and will continue to be developed in the near future. Many interesting experiments have been done and were reviewed in section 4. As sensitizers, many types of dyes and QDs have been used. The sensitizing dyes were usually attached onto the surfaces of the titania nanomaterials, but they might also be the components of the electrolytes surrounding the photoanodes. In the latter case, sensitizing dyes were degraded (as the pollutants) or decomposed (as the fuels) to generate electricity and/or hydrogen. Among sensitizing QDs, the most preferable one is CdSe QD. With respect to photocorrosion, this QD is more stable than CdS and CdTe QDs, but there still exists the question: how stable is it, how long is the lifetime of a QDSSC, for example, using a CdSe QD? In general, a QDSSC as well a PC or PEC cell sensitized by a QD can achieve a high efficiency only if it has a suitable complex structure composed from different elements whose working mechanisms are based on different physical phenomena and processes or on catalytic reactions at the interfaces between the electrolyte and the electrodes. Lots of physical and chemical fundamental research works should be done in order to achieve success in fabricating perfect QD sensitized PEC cells for solar energy conversion or for pollutant degradation. In general the working mechanisms of visible light responsive QD sensitized titania-based nanostructures are more complicated than those of doped titania nanomaterials. In most works reviewed in section 4 the QD sensitized titania-based nanostructures were prepared mainly on the basis of pure titania NPs or NCFs. Recently the technology for fabricating titania nanotube, nanowire and nanorod arrays was elaborated. The replacement of NPs or NCFs by one-dimensional titania nanomaterials would enhance the PC activity of the prepared photoanodes. The SPR in the metallic NPs deposited onto the surfaces of titania-based nanomaterials or nanostructures would significantly enhance their PC activities with respect to the sunlight illumination. In brief, a promising and wide field of fundamental physical and chemical research on visible light responsive QD-sensitized titania-based nanostructures for photovoltaic, photocatalytic and photoelectrochemical applications was being opened.

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