Effects of photocatalytic activity of metal and non-metal doped TiO$_2$ for Hydrogen production enhancement - A Review

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Abstract. Titanium dioxide TiO$_2$ is well-known materials that has become an efficient photocatalyst for environmental sustainability. Known as solar driven catalysis, TiO$_2$ is considered as the most promising way to alleviate environmental issues caused by the combustion of fossil fuels and to meet worldwide demands for energy. Much effort has been concerned on TiO$_2$ band gap modification to become a visible-light-activated photocatalysts of TiO$_2$ because it can only be excited by UV light irradiation due to its large band gap. Modifications like metals and nonmetals doping has been proposed in the past decades. This review surveys recent advanced preparation methods of doped-TiO$_2$ including various types of doping methods for various types of dopants and provides general review on further modifications. The characterizations techniques used in order to determine the structural, morphological and optical properties of modified TiO$_2$ is also discussed. Further, a new method of TiO$_2$ modification is proposed in this mini review paper.

1. Introduction
Titanium dioxide (TiO$_2$) or commonly known as titania is the most effective photocatalyst for air and water purification and self-cleaning surfaces, and also widely used for energy-related fields especially in water splitting under visible light irradiation [1-3]. According to previous research, TiO$_2$ has been proven to be the most efficient and economic photocatalyst due to its capability to completely mineralize contaminants [4-5], low cost material, superhydrophilicity [6,8] for self-cleaning function and antibacterial agent [9], non-toxicity, and has high oxidative abilities [10-12].

Photocatalysis was first discovered by Fujishima in 1970’s and later called as Honda-Fujishima Effect. A strong oxidation and reduction power of TiO$_2$ was realized through a simple experiment of TiO$_2$ electrode in an aqueous solution exposed to strong light. Photoinduced decomposition of water on TiO$_2$ electrodes are reported as a gas bubbles evolved from the surface of electrodes after being exposed to strong light. Analogically, photocatalytic reaction on TiO$_2$ was found to be similar with photosynthesis – as illustrated in Figure 1; light is used as an energy that enables to break water molecule into hydrogen and oxygen [13].
Following from Honda-Fujishima effect, the applications of TiO$_2$ photocatalyst are elevates rapidly in various sector such as in photoelectrolysis to generate hydrogen energy from water splitting [14-21], anti-corrosion coating material [22], and an organic pollutant degradation to tackle environmental issues [23-27]. In general, when TiO$_2$ surface was irradiated with ultraviolet light there will be two types of photochemical reaction to occur. First, photo-induced redox reactions of adsorbed substances, and also photo-induced hydrophilic conversion of TiO$_2$ itself. Despite all the interesting features in TiO$_2$, its large energy band gap is in range 3.0 eV (rutile) to 3.5 eV (anatase) corresponding to wavelengths of 385 and 410 nm respectively – which allows the absorption of light in ultraviolet range only [28]. Besides, fast recombination of electrons and holes, slow charge carrier transfer and also requires high reproduction cost limit the efficiency of photocatalytic activity of TiO$_2$ [29]. Due to this flaw, various attempts has been done in order to modified the band gap of TiO$_2$; with such it will broaden the light absorption range mainly in visible light range that corresponds about 40 % of light spectrum [28,30-33]. The photocatalytic activity under simulated sunlight irradiation is determine from the band gap, the valence band VB and covalence band CB edge positions of photocatalyst [17].

Many approach have been done in previous research to reduce the intrinsic band gap of titania including cations (mainly transition metals or rare earth metal ions) or anions doping into TiO$_2$ lattice host material [12,28,34-38].

2. Preparation of Doped TiO$_2$
There are various chemical and physical methods available on preparing doped-TiO$_2$ - either anatase or rutile structure. Those methods including ion-assisted sputtering, plasma, ion-implantation, chemical vapor deposition (CVD) and sol-gel to enhance the photocatalytic effect in the visible light region. A list of doped TiO$_2$ and methods of its preparation are shown in Table 1(a) and Table 1(b) [10,39-42].
2.1 TiO\textsubscript{2} Doped with Metal Species
Metal doped TiO\textsubscript{2} especially transition metal has been extensively investigated over the past decades for enhancing its photocatalytic performance on the degradation of various organic pollutants under visible irradiation. This modification is done to extend the optical absorption of TiO\textsubscript{2} to visible light.

Table 1(a). Dopants and Preparation Methods of metal-doped-TiO\textsubscript{2} photocatalysts.

| Doped Element | Preparation Method                                                                                                                                                                                                                           | Reference |
|---------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| Pd            | Synthesized using alkaline route of sol-gel method. The doped materials were obtained by simultaneous gelation of both precursors in the sol–gel process. Absolute ethanol, min. 99.8 vol %, was used as solvent for both titania and palladium precursors. The hydrolysis reaction took place in the presence of the water, added in substoichiometric quantity, in a closed system, in nitrogen atmosphere, under vigorous stirring. The nitric acid, HNO\textsubscript{3} 65 % Merck, was used as catalyst to obtain a final pH of the sol in the range 3-3.5. | [39]      |
| Fe            | Titanium tetraisopropoxide, 97% pure, ethanol, diethanolamine and iron nitrate, 98% pure, were used for preparation of thin films. Indium doped tin oxide (SnO\textsubscript{2}:In) conducting glass was used as substrate. A transparent gel solution of doped/ undoped TiO\textsubscript{2} was prepared by mixing of 3 ml TTIP and calculated amount of iron nitrate in 20 ml ethanol in the presence of diethanolamine. The solution was stirred for 4 hours at room temperature to enhance the reaction rate between diethanolamine and TTIP and finally it gets converted into gel. This gel solution was applied on nearly two third area of the conducting glass substrate and uniformly coated with spin coating unit. After each successive layer the film was allowed to dry for 10 min at 80 °C. Final sintering was done at 500 °C for 2 h. | [40]      |

It is reported that metal doping has shown photocatalytic activities at both UV and visible light range [43]. Furthermore, metal-doped TiO\textsubscript{2} will caused many drawbacks including dopant insolubility, thermal instability during the process, phase transformation among the titania polymorphs, the increase of carrier-recombination centers, and the alteration of charge carrier diffusion length.

2.2 TiO\textsubscript{2} With Non-metal Species
Nonmetal-doped TiO\textsubscript{2} is reported as the most promising photocatalysts candidates [44]. An extensive research of nonmetal-doped TiO\textsubscript{2} photocatalysts was widely carried out since the early 1990s [5,8]. Among all the nonmetal-doped TiO\textsubscript{2} photocatalysts, nitrogen-doped TiO\textsubscript{2} is the most studied material [45]. In addition, several other visible-light active materials, such as carbon C, F and S, doped TiO\textsubscript{2} were reported [19].
### Table 1(b). Dopants and Preparation Methods of non-metal-doped-TiO$_2$ photocatalysts.

| Doped Element | Preparation Method | Reference |
|---------------|--------------------|-----------|
| Glass Substrate | The three components were used in the preparation of the TiO$_2$ Sol-Gel films it can be explained as follows: Titanium Isopropoxide (TIP), Acetic acid and Ethanol. TiO$_2$ thin films are prepared by Sol-Gel spin-coating method using 50 ml of Ethanol and allowed to mix for 50 min, measure 5 ml of acetic acid with a pipette into Ethanol and stir by using a magnetic stirrer it for 5 min or at least 3 min, and measure 6.3 ml of TIP was added by pipette to a beaker containing a mixture of glacial acetic acid and ethanol that had been mixed for five minutes. The mixture was continually stirred using a magnetic stirrer addition and for a further two minutes after addition of the precursor. The concentration was altered in order to assess the effects of ratios and concentration. Glass slide coated with transparent conducting indium tin oxide (ITO) films were used as substrates. | [10] |
| Zz | Doping was performed by an incipient wet impregnation method as the N, C and S-sources. TiO$_2$ Degussa P25 and appropriate amounts of N, C and S were mixed with specific volumes of doubly distilled water and stirred for 1 hour. During this period, the mixture changed color into a yellowish/ greyish white depending upon the anion concentration. Then, the prepared photocatalysts were washed with water three times, heat-treated at 373 K for 24 hours to eliminate water, calcined at three different temperatures in the range 623-973 K for 1, 3 and 5 hours, ground and sieved. | [41] |
| N, S, C | TiO$_2$ nanostructures were prepared using LPD method. ITO substrates underwent standard cleaning procedure where they were cleaned using acetone and ethanol in sequence. The growth process was carried out under room temperature. The as prepared nanostructured TiO$_2$ was rinsed and dried before it was annealed at 400 °C for 30 minutes. Growth of the TiO$_2$ nanoparticles was started with hydrolysis of the metal fluoro cation used ((NH$_4$)$_2$TiF$_6$) with boric acid was used to scavenge the fluoro cation left. TiO$_2$ nanoparticles film formed on the surface was then subjected towards annealing process to purify the metal oxide nanoparticles produce and to remove organic materials left during the hydrolysis process. The treated samples were then subjected towards heating at 100 °C for 15 minutes to remove any hydroxyl compounds. | [42] |

The three components were used in the preparation of the TiO$_2$ Sol-Gel films it can be explained as follows in Figure 2.
Figure 2. Procedure of doped-TiO$_2$ via Sol-Gel method.

TiO$_2$ thin films are prepared by sol-gel spin-coating method using 50 ml of ethanol and allowed to mix for 50 min, measure 5 ml of acetic acid with a pipette into ethanol and stir by using a magnetic stirrer for 3 to 5 min. The mixture was continually stirred using a magnetic stirrer addition and for a further two minutes after addition of the precursor. The sol-gel concentration was altered in order to assess the effects of ratios and concentration. The effects of altering molar ratios of acid are investigated. The Sol-Gel manufactured due to the method described above was immediately used to produce coating on the various substrates. Thin films of TiO$_2$ were deposited by spin coating method using a standard photoresist spinner [1,10,46].

In short, the Sol-Gel process is one of the versatile methods in preparing Nano-size materials. This technique does not require a complicated instrument which provides a simple and easy means for preparing Nano-size particles. The incorporation of an active dopant in the Sol-Gel during the gelation stage allows the doping elements to have a direct interaction with support, therefore, the material possesses catalytic or photocatalytic properties. Titanium precursor, such as titanium isopropoxide (TIP), tetrabutyl orthotitanate (TBOT), titanium tetra chloride, is mixed with dopant precursor dissolved in alcohol, followed by hydrolysis performed at the room or elevated temperature. The precipitate is dried usually at temperature range from 80 to 110°C, pulverized to obtain xerogel and calcinated in air at temperature from 200 to 600°C [46].

3. Morphological Surface and Photocatalytic Analysis

Among metal dopants as mentioned previously, Fe (III) ions as the most favourable dopant due to its unique electronic structure and its similar size with titanium (IV), Ti$^{4+}$ ions [40]. The energy level of the Fe$^{3+}$/Fe$^{2+}$ couple is only just greater than the titania conduction band and the energy level of the Fe$^{3+}$/Fe$^{2+}$ couple is just above the valance band [47]. This useful electronic states of iron ions in titania results in formation of efficient trapping sites for electrons and holes [48].
3.1 Crystalline structure of doped-TiO2

Aside of types of dopant substitute into TiO2 lattice structure, the annealing temperature of TiO2 thin films also plays a crucial role in order to produce a rutile or anatase semiconductor. A pure TiO2 films is prepared at various annealing temperature from 300 to 800 °C. Figure 3 shows the X-ray diffraction XRD patterns of the prepared samples. It was found that the pure TiO2 films with anatase phase increase when annealing temperature increased. The pure TiO2 films formed of anatase phase show a very high efficiency photocatalytic activity due to their large internal surface. Both the optical properties and the photocatalytic activity of TiO2 coatings depend strongly on the crystalline phase, the crystallite size and the porosity of the coatings. Moreover, the TiO2 films formed of rutile phase when the sample annealed at a temperature more than 700 °C [6].

Figure 4 shows the XRD pattern of pure TiO2 and 0.2 at.% Fe doped TiO2 films at final sintering temperature at 500 °C for 2 h. The obtained patterns shows a predominance of sharp, intense peak corresponding to underlying SnO2:In layer on the substrate. From the pattern, weak intensity peaks corresponding to anatase phase of TiO2 is obtained for all samples of Fe3+ doped TiO2. Besides, a high crystalline material was obtained for 0.2 at.% Fe doped TiO2. By using Scherrer’s equation (D = Kλ/βcos θ), the crystallite size was calculated and the sizes of TiO2 particles are confirmed in nanosize for different concentration of dopant [40].

As for non-metal doped TiO2, a carbon-doped TiO2 thin films were prepared by hydrothermally synthesized using Ti(SO4)2 and glucose as titania and carbon resources for 12 to 48 hours [19]. The obtained carbon-TiO2 nanocrystals display higher energy conversion efficiencies than pure TiO2 when applied as the photo-anode materials in dye-sensitized solar cells DSSCs. Based on the combinational analyses on dye adsorption efficiency, photoluminescence and electron lifetime of TiO2, the retarded hole-electron recombination rate and the negatively shifted flat band potential were revealed as the main reasons for the improved energy conversion efficiency.

XRD pattern in Figure 5 shows an obvious anatase phase peaks in each sample. This proves that the presence of glucose does not cause the change of crystalline phase. The calculated crystallite size of carbon-TiO2 is in the range of 14 to 19 nm that is smaller than that of pure TiO2 (24 nm). Smaller size of TiO2 nanoparticles will improved particle dispersity for conversion efficiency advancement.
Figure 3. X-ray diffraction patterns of pure TiO$_2$ films after annealed at different temperature [6].

Figure 4. XRD patterns of pure TiO$_2$ (undoped) and doped 0.2 at.% Fe thin films deposited on conducting glass plate [40].
Figure 5. X-ray diffraction patterns of pure TiO$_2$ carbon-doped TiO$_2$ films [19].

Figure 6. UV–vis–NIR diffuse reflectance spectrophotometric curves for pure and Pd-doped-TiO$_2$ nanoparticles [52].
Figure 7. UV-vis absorption curves of Zn-doped-TiO2 films [53].

The band gap of the TiO2:Zn2+ is decreased with increasing Zn2+ dopant. Since the valence band edge of TiO2 material is dominated by O 2p, and the conduction band edge is formed from Ti 3d, some of the new occupied molecular orbitals located below the conduction band of TiO2 would be formed when Zn2+ ions were doped into TiO2 lattice. The decreased of band gap would likely cause to the charge transfer from the dopant energy level Zn2+ to the conduction band of TiO2 [47]. Besides, other dopant that shows an interesting result is carbon. C-doped-TiO2 proved that the particles are crystalline with spherical morphology, high surface area and an optical band gap of 2.79 eV for C-TiO2 annealed at 400 °C as reported by Warkhade et. al. [11].

4. Conclusion

The modification methods of x-doped-TiO2 have been discussed in this review paper. Between two types of dopant elements that are metal and non-metal, non-metal (anions) shows a significance role in order to enhance the performance of TiO2 photocatalyst. The biggest challenge involving TiO2 as photocatalysts is to increase its spectral sensitivity to visible light. A new dopants and new method in preparing modified structure of TiO2 would be the next approach of future research. With such, a new applications of TiO2 in various sector would be revealed. Currently, the major problem with doped TiO2 may be the loss of photoactivity during recycling and long-term storage. It is seems that the efficiency of doped-TiO2 under visible light strongly depended on the preparation method used.

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References

[1] R Dholam, N Patel, M Adami and A Miotello 2008 Physically and chemically synthesized TiO₂ composite thin films for hydrogen production by photocatalytic water splitting. *Int. J. Hydrogen Energy* **33**(23) 6896–6903

[2] M Ni, M khla, D Y C Leung and K Sumathy 2007 A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production. *IJJCE* **11** 401–425

[3] Z Zhu, C Kao, B Tang, W Chang and R Wu 2016 Efficient hydrogen production by photocatalytic water-splitting using Pt-doped TiO₂ hollow spheres under visible light. *Ceram. Int.* **42**(6) 6749–6754

[4] R J Tayade, S Technol and A Mater 2007 Photocatalytic degradation of dyes and organic contaminants in water using nanocrystalline anatase and rutile TiO₂. Photocatalytic degradation of dyes and organic contaminants in water using nanocrystalline anatase and rutile TiO₂

[5] C S Turchi 1990 Photocatalytic Degradation of Organic Water Contaminants: Mechanisms Involving Hydroxyl Radical Attack. *192* 178–192

[6] S Lien and J Jhu applications 2–4

[7] H Kong 2014 Light-induced super-hydrophilicity and photocatalytic activity of mesoporous TiO₂ thin films. *Appl. Sci. 2014* no. May 2002

[8] M Machida, K Norimoto and T Watanabe 1999 The effect of SiO₂ addition in super-hydrophilic property of TiO₂ photocatalyst. *4*, 2569–2570

[9] A Zaleska 2008 Doped-TiO₂ : A Review (1) 157–164

[10] V S Process, M H Shinen, K I Ajeel and F A Rasin 2001 Preparation of Titanium Dioxide (TiO₂) no. Rancourt 1987 1–9

[11] S K Warakhe, G S Gaikwad, S P Zodape, U Pratap and A V Maldhure 2017 Low temperature synthesis of pure anatase carbon doped titanium dioxide: An efficient visible light active photocatalyst. *Mater. Sci. Semicond. Process. 63* (November 2016) 18–24

[12] A O Technologies 2014 The Role of Non-Metal Doping in TiO₂ Photocatalysis. The Role of Non-Metal Doping in TiO₂ Photocatalysis no. April

[13] K Hashimoto, H Irie and A Fujishima 2005 TiO₂ Photocatalysis: A Historical Overview and Future Prospects. *Jpn. J. Appl. Phys.* **44**(12) 8269–8285

[14] B Gupta and A A Melvin 2017 TiO₂ / RGO composites: Its achievement and factors involved in hydrogen production. *Renew. Sustain. Energy Rev.* **76** April 1384–1392

[15] Y C Leung, X Fu C Wang, M Ni and M K H Leung 2010 Hydrogen Production over Titania - Based Photocatalysts. Hydrogen Production over Titania-Based Photocatalysts no. April 2014

[16] S Escobedo, B Serrano, A Calzada, J Moreira and H De Las 2016 Hydrogen production using a platinum modified TiO₂ photocatalyst and an organic scavenger. *Kinetic modeling Fuel* **181** 438–449

[17] F Opoku, P Govender, F Opoku, K K Govender, C Gertina and C Elizabeth 2017 Recent Progress in the Development of Semiconductor-Based Photocatalyst Materials for Applications in Recent Progress in the Development of Semiconductor-Based Photocatalyst Materials for Applications in Photocatalytic Water Splitting and Degradation no. July

[18] T U Wien 2016 Hydrogen production by photocatalytic water-splitting on Pt-doped TiO₂ – ZnO under visible light. *J. Taiwan Inst. Chem. Eng.* no. November

[19] A Lin, D Qi, H Ding, L Wang, M Xing, B Shen and J Zhang 2017 Carbon-doped titanium dioxide nanocrystals for highly efficient dye-sensitized solar cells. *Catal. Today* **281** 636–641

[20] P Wang, S Zhan, Y Xia, S Ma, Q Zhou and Y Li 2017 Applied Catalysis B: Environmental. The fundamental role and mechanism of reduced graphene oxide in rGO / Pt-TiO₂ nanocomposite for high-performance photocatalytic water splitting. *207* 335–346

[21] F Song 2017 Metal – Organic frameworks and their derivatives for photocatalytic water
splitting inorganics Metal – Organic frameworks and their derivatives for photocatalytic water splitting no. July

[22] K Nakata and A Fujishima 2012 Reviews TiO 2 photocatalysis : Design and applications Journal of Photochemistry and Photobiology C : Photochemistry 13 169–189

[23] W Kim, G Jang, J Lee and D Rhee 2014 Degradation of Methylene Blue by Titania doped with Transition Metal and Nitrogen Energy Procedia 61 2456–2459

[24] M Reza, D Khaki, M Saleh, Aziz, A Aziz, A Raman, W Mohd and A Wan 2017 Application of doped photocatalysts for organic pollutant degradation - A review J. Environ. Manage. 198 78–94

[25] S Bagheri and N M Julkapli 2016 ScienceDirect Synergistic effects on hydrogenated TiO 2 for photodegradation of synthetic compounds pollutants Int. J. Hydrogen Energy 41(33) 14652–14664

[26] P Wen, M Hayrie, M Hatta, S Teng, L Yuliati and S Ling 2017 Journal of Photochemistry and Photobiology A : Chemistry Photocatalytic degradation of photosensitizing and non-photosensitizing dyes over chromium doped titania photocatalysts under visible light Journal Photochem. Photobiol. A Chem. 332 215–223

[27] B Appavu and S Thiripuranthagan 2017 Journal of Photochemistry and Photobiology A : Chemistry Visible active N , S co-doped TiO 2 / graphene photocatalysts for the degradation of hazardous dyes Journal Photochem. Photobiol. A Chem. 340 146–156

[28] Z Islam, S Nagpure, D Y Kim and S E Rankin 2017 Synthesis and Catalytic Applications of Non-Metal Doped Mesoporous Titania Synthesis and Catalytic Applications of Non-Metal Doped Mesoporous Titania Inorganics 5(1) 15

[29] Ge, J Cai, J Iocozzia, C Cao, S Zhang, K Zhang, Y Lai and Z Lin 2016 Science Direct A review of TiO 2 nanostructured catalysts for sustainable H 2 generation Int. J. Hydrogen Energy 42(12) 8418–8449

[30] H Yan, X Wang, M Yao and X Yao 2013 Band structure design of semiconductors for enhanced photocatalytic activity: The case of TiO2 Prog. Nat. Sci. Mater. Int. 23(4) 402–407

[31] Ceylan, C Ozgit-Akgun, T S Erkal, I Donmez, R Garifullin, A B Tekinay, H Usta, N Biyikli and M O Guler 2013 Size-controlled conformal nanofabrication of biotemplated three-dimensional TiO2 and ZnO nanonetworks Sci. Rep. 3 2306

[32] A V Rosario and E C Pereira 2014 Applied Catalysis B : Environmental The role of Pt addition on the photocatalytic activity of TiO 2 nanoparticles : The limit between doping and metallization Applied Catal. B, Environ. 144 840–845

[33] O Van Overschelde, R Snyder and M Wautelet 2007 Crystallisation of TiO2 thin films induced by excimer laser irradiation Appl. Surf. Sci., 254(4) 971–974

[34] Lei, Y Su, M Zhou, X Zhang and X Chen 2007 Fabrication of multi-non-metal-doped TiO2 nanotubes by anodization in mixed acid electrolyte Mater. Res. Bull. 42(12) 2230–2236

[35] K Siuzdak, M Abbas, L Vignau, M Devynck, G V Dubacheva and A Lisowska-Oleksiak 2012 Application of non-metal doped titania for inverted polymer solar cells J. Appl. Phys. 112(12)

[36] C Di Valentin and G Pacchioni 2013 Trends in non-metal doping of anatase TiO 2 : B , C , N and F 206 12–18

[37] K Kadakia, M K Datta, O I Velikokhatnyi, P Jampani, S K Park, S J Chung and P N Kumta 2014 High performance fluorine doped (Sn,Ru)O2 oxygen evolution reaction electrocatalysts for proton exchange membrane based water electrolysis J. Power Sources 245 362–370

[38] Linnik, N Shestopal, N Smirnova, A Eremenko, O Korduban, V Kandyba, T Kryshchuk, G Socol, N Stefan, G Popescu-pelin, C Ristoscu and I N Mihailescu 2015 Correlation between electronic structure and photocatalytic properties of non-metal doped TiO 2 / ZrO 2 thin films obtained by pulsed laser deposition method Vacuum 114 166–171
[39] M Cris, A Bra, D Cris, N Dra, A Ianculescu, D Mardare, D Luca, V Marinescu and A Moldovan 2008 Crystallization study of sol–gel undoped and Pd-doped TiO$_2$ materials Journal of Physics and Chemistry of Solids 69 2548–2554

[40] A P Singh, S Kumari, R Shrivastav, S Dass and V R Satsangi 2008 Iron doped nanostructured TiO$_2$ for photoelectrochemical generation of hydrogen Int. J. Hydrogen Energy 33(20) 5363–5368

[41] Y Yalçin, M Kiliç and Z Çinar 2010 The role of non-metal doping in TiO$_2$ photocatalysis J. Adv. Oxid. Technol. 13(3) 281–296

[42] A A Umar, M Yusr, A Rahman, S Khatijah, M Saad and M M Salleh 2012 Effect of NH 3 Concentration on the Performance of Nitrogen doped TiO$_2$ 2 Photoelectrochemical Cell Int. J. Electrochem. Sci 7 7855–7865

[43] J Park, K Choi, J Lee, C Hwang, D Choi and J Lee 2013 Fabrication and characterization of metal-doped TiO$_2$ nanofibers for photocatalytic reactions Mater. Lett. 97 64–66

[44] T Teka 2015 Current State Of Doped-TiO$_2$ Photocatalysts And Synthesis Methods To Prepare TiO$_2$ Films : A Review J. Electrochem. Sci 7 855–865

[45] S Walck 2014 Photochemical Activity of Nitrogen-Doped Rutile TiO$_2$ ( 110 ) in Visible Light Mater. Lett. 97 64–66

[46] A Zaleska 2008 Doped-TiO$_2$: A Review Recent Patents Eng., 2(3) 157–164

[47] T T Loan, V H Huong, V T Tham and N N Long 2017 Effect of zinc doping on the bandgap and photoluminescence of Zn 2 + doped TiO$_2$ 2 nanowires 2–7

[48] A Zarubica, T Minovi and N Abazovi 2016 Journal of the European Ceramic Society Iron doped anatase for application in photocatalysis 2991–2996

[49] S Chen 2014 Band gap narrowing of TiO$_2$ doped with Ce probed with X-ray absorption spectroscopy 2–5

[50] T Morikawa and T Central 2001 BandGap Narrowing of Titanium Dioxide by Nitrogen Doping Japanese Journal of Applied Physics no. May 2016 2–5

[51] C O Ayieko, R J Musemb, S M Waita, B O Aduda and P K Jain 2012 Structural and Optical Characterization of Nitrogen-doped TiO$_2$ Thin Films Deposited by Spray Pyrolysis on Fluorine Doped Tin Oxide ( FTO ) Coated Glass Slides 2(3) 67–72

[52] A Narayan, N Hannabard and S Woo 2016 A comparative study of the effect of Pd-doping on the structural, optical and photocatalytic properties of sol–gel derived anatase TiO$_2$ 2 nanoparticles Ceram. Int., 42(10) 1200–12026

[53] L Qiao, F Xie, M Xie, C Gong, W Wang and J Gao 2016 Characterization and photoelectrochemical performance of Zn-doped TiO$_2$ 2 films by sol–gel method Trans. Nonferrous Met. Soc. China 26(8) 2109–2116