Potential Dopant in Photocatalysis Process for Wastewater Treatment—A Review

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Abstract. Nowadays, too much pollution has happened around us, and one of them is water pollution, which each day has become more severe and worse. One of the sources of water pollution comes from the industry that has used dyes either excessively or not. In case of that, the wastewater needs to be treated before released to the river or environment. In this paper, a review of the wastewater treatment using dopants such as nitrogen and magnesium, will be discussed.

1. Introduction

Water pollution have become a serious issue nowadays especially in the textile industry, printing industry, food manufacturing and also cosmetic industry. These industries contribute to water pollution as they release wastewater that contains azo dyes. Azo dyes are widely used as the pigmentation and bright color that is highly demanded especially by the textile industry. Based on research, about 10% to 15% of dyes used are released together with the wastewater and due to the complex chemical structure of dyes, causing the difficulties in wastewater treatment [1].

The structures of azo dyes may contain with one or more azo group (-N=N-) as a chromophore in the molecular structure. The azo dyes are synthesized from aromatic compound and basic aqueous solution (presence of N=N may reduce the unpaired electron pairs in nitrogen atoms). Most of them belong to the non-biodegradable and recalcitrant type of water pollutant, which cause activated sludge treatment methods inadequate [2]. From the absorption spectra pattern done by the previous researchers, the dyes decomposed quickly and no new absorption bands appeared in both visible and ultraviolet regions, which indicates that no aromatic moieties and other similar intermediates were produced [30].

The uncontrollable releasing of wastewater contaminants with dyes can cause environmental issues including the reduction of light absorption due to the organisms that inhabit the aquatic environments and production of different amines under anaerobic conditions [1].

One of the popular methods is including the photocatalysis process that has been widely used in the degradation of azo dyes. Photocatalysis was known to be a friendly environmental process which will totally degrade the pollution into water and carbon dioxide [3]. In photocatalysis, titanium dioxide is often used as the catalyst due to the cheap raw materials, easy to obtain and also environmental friendly.

A non-metal dopant, as an example, nitrogen is considered as the most effective dopant for photocatalysis to be incorporated with TiO2 as the size is smaller and the source is cheaper. Dopant is an impurity that added in controlled amount to a pure semiconductor to change its electrical properties.
While, photocatalysis is the process when a light source interacts with the semiconductor surface that known as photocatalysts (figure 1). Besides nitrogen, magnesium also can be an example that can be choose as effective dopant. By inserting metal ions into TiO$_2$ structure can decrease the band gap and from the research, it is found that metals are able to lower the electron-hole recombination rate and trap the electrons [4]. Besides that, there were proven that as the particle size changed, the specific surface area, charge-carrier dynamics and light absorption efficiency of TiO$_2$ nanoparticles also changed [31]. While the particle size decreases obviously to an average of 100 nm and a small amount of particles about 20 nm can be seen on TiO$_2$ [32]. In this paper, the review about the nitrogen and magnesium as a dopant will be discussed.

![Figure 1. Photocatalysis process](image)

2. Nitrogen as dopant
Nitrogen has been widely used as a dopant due to the comparable size and electronegativity to the oxygen and it is the most suitable element to reduce the band gap width of TiO$_2$ [5]. Zhou et al, (2011), reported that only anatase phase occurred when TiO$_2$ is doped with nitrogen and the photocatalytic activity for degradation of methyl orange under UV-visible and visible light is improved compared to pure TiO$_2$ and P25 [6]. A research conducted by Yang et al, (2010), also showed that the photocatalytic activity can be improved by using N-doped where the incorporation of N atom into TiO$_2$ molecule has shifted the UV region to the visible light region [7]. They also believed that the narrowing band gap of N-doped TiO$_2$ resulting in the visible light activities can cause formation of oxygen vacancies. The researchers found only TiO$_2$ in pure anatase presence after the doping process. The molar ratio of nitrogen to TiO$_2$ may also affect the doping effect and the study reported that the optimum molar ratio of nitrogen to TiO$_2$ is 1.0, which also gives the highest rate of photocatalytic activity.

A series of nitrogen doped titanium dioxide produced by using two-steps hydrolysis-calcination method was conducted by Wang et al, (2007)[8]. By going through the hydrolysis process, the time consumed is shortened compared to the traditional one. The samples were analysed using XRD, UV-vis diffuse reflectance spectra, FTIR and XPS. Pure anatase has been obtained from the doping technique. The UV-Vis diffuse reflectance/absorbance showed slight increase in absorption and the band gap decreased from 3.12 to 2.22 eV for pure TiO$_2$ and N-doped TiO$_2$ respectively. The photocatalytic activity for doped titanium dioxide is found to be better than the pure titanium dioxide and can be performed under visible light irradiation.

Lindgren et al, (2003), has prepared samples of nanocrystalline porous nitrogen doped titanium dioxide (TiO$_2$) thin films by DC magnetron sputtering and the results have shown that the films were porous and displayed rough surfaces with sharp, protruding nodule that having a crystal structure which consists of rutile and anatase [9]. Each nodules were estimated to be from 100 to 500 nm in size. The N-TiO$_2$ showed an optical response in the 400 to 535 nm wavelength and this new band gap states were
created through the doping which also improved the photoresponse for white light at the expense of some losses of UV response.

The optical band gap of N-TiO$_2$ was found to be 2.8 eV compared to the band gap of pure TiO$_2$ [10], by using sol gel acid catalysed reaction. The shifted band gap showed that nitrogen doped TiO$_2$ is proved to be significant on the visible light absorbance. This shifted band gap is presumably due to the substitution of the lattice oxygen by nitrogen and oxynitride centre is formed. The SEM analysis of nitrogen doped TiO$_2$ showed smaller size particles compared to the pure TiO$_2$. This is confirmed when the particle size is calculated by using Scherrer’s equation and the average sizes are 17.43 and 24.07 nm for the N-TiO$_2$ and pure TiO$_2$ respectively. According to the quantum size effect theory, the smaller the semiconductor particle size, the wider the band gap of photocatalytic activities of N-TiO$_2$ and pure TiO$_2$ when evaluated by the degradation of 5 ppm of crystal violet (CV) dye under the visible light. The result showed that N-TiO$_2$ has high efficiency of 78% but pure TiO$_2$ shows 15% photocatalytic efficiency under the visible light. The high catalytic efficiency of photocatalyst can be attributed to the small crystallite size, high crystallinity and intense light absorption in the visible light region. Based on the experiment conducted by Darzi et al. (2012), the conclusion is made when the doping nitrogen with TiO$_2$ causes the size of crystallites become smaller compared to the pure TiO$_2$ [10]. The band gap of N-TiO$_2$ is also found to be shifted to visible light region which helps the photocatalytic activity of CV under the visible light.

A special structure called oxynitrides will be formed when oxygen species is substituted by nitrogen species and it can absorb visible light [11]. Huang et al. (2007), prepared samples of N-TiO$_2$ and calcined at different temperature between 400°C and 700°C. All the samples underwent washing process except for the sample calcined at 400°C [12]. The UV-Vis diffuse reflectance spectra showed that sample calcined at 400°C have a strong absorption of visible light compared to the other samples. For photocatalytic activity, the N-doped TiO$_2$ showed higher reaction than the pure TiO$_2$. The N-doped TiO$_2$ is also found to have high absorption activity for the light at 550 nm wavelength.

N-doped TiO$_2$ has been synthesised with different nitrogen concentrations by using mild hydrothermal method. The experiment is conducted by Xu et al. (2015), and the XRD patterns showed only all anatase single phase and no peaks of nitrogen compounds were found [13]. They assumed that the nitrogen species might be embedded in the structure of TiO$_2$ and located at interstitial or substitutional sites of the TiO$_2$ lattice. As the N to Ti ratio is increased, the anatase peak became slightly broader and this showed that the crystallisation of TiO$_2$ became weaker after the nitrogen doping. The morphologies of pure and N-TiO$_2$ showed that the samples were not affected by nitrogen doping. The morphology of samples showed in sphere shape. The band gap values of the samples showed 3.20, 3.00, 2.96, and 2.92 eV respectively for the TN-0, TN-4, TN-1 and TN-3. The band gap was narrowed and proved that the nitrogen atoms were successfully inserted into the TiO$_2$ structure.

The synthesised N-doped TiO$_2$ by Caratto et al. (2012), is prepared by using sol-gel and the photocatalyst is calcined at 700°C, while the undoped TiO$_2$ is calcined at 350°C [14]. The phase identification performed by XRD showed that the samples at 350°C were all in anatase phase, while the samples that calcined at 700°C showed the coexistence of anatase, rutile and a third phase called titanium nitride (osbornite-type). They reported that the anatase structure has been stabilised by N doping and high temperature treatments which led to a reduction of N solubility. SEM analysis showed the pure TiO$_2$ having rounded shape and form sponge-like aggregates, while N-TiO$_2$ forms lamellar isolated aggregates. They claimed that the variation of N$^+$ ions does not give any significant morphological change, even at higher magnification. This is because, the shape stability of TiO$_2$ nanoparticles is highly dependent on surface chemistry and the synthesis conditions. According to theoretical models, in the case of hydrogenated, hydrogen-rich and hydrated surfaces, the shape of anatase and rutile nano particles vary very little with surface chemistry where only slight changes can be seen. However, when the condition is in poor hydrogen and oxygenated surfaces, and there is a presence of base such as NH$_3$, the nanocrystals of both polymorphs become elongated and could lead to the formation of lamellar aggregates. The band gap of nitrogen doped with NH$_3$ of 3%, 7%, 10%, and
15% showed 3.123, 3.092, 3.054 and 3.009 eV respectively which is narrowed when compared to the pure TiO$_2$ with the band gap of 3.642 eV. From these results, they claimed that the properties of TiO$_2$ have been improved by nitrogen doping and could be used in more severe environments, which are commonly occurred in the chemical plants.

Thus, based on the previous study of nitrogen doping, the structure of TiO$_2$ could be improved, where the band gap can be reduced with the insertion of nitrogen as dopant. Thus the visible light can be used to activate the photocatalysis activity.

**Table 1. Summary of all the findings of using nitrogen as the dopant**

| Method | Dopant | Performance of modified photocatalyst                                                                 | References |
|--------|--------|------------------------------------------------------------------------------------------------------|------------|
| Sol-gel acid catalysed reaction | Nitrogen | • Optical band gap at 2.8 eV (lowered compare to pure TiO$_2$).  
• Average size of crystal 17.43 nm.  
• High efficiency of 78 % of photocatalytic activity. | [10]       |
| Two-step hydrolysis-calcination | Nitrogen | • Band gap reduced from 3.12 to 2.22 eV.  
• N-TiO$_2$ performed better photocatalytic compared to pure TiO$_2$. | [15]       |
| Thin films by DC magnetron sputtering | Nitrogen | • Photocatalyst consist of anatase and rutile.  
• N-TiO$_2$ showed response to 400 to 535 nm wavelength (visible light range).  
• Films having rough surface and nodules were estimated around 100 to 500 nm in size. | [16]       |
| Sol-gel | Nitrogen | • N-TiO$_2$ has optical response at 550 nm (visible range).  
• Photocatalytic activity showed higher reaction compare to pure TiO$_2$. | [17]       |

**Table 2. Method and performance of modified TiO$_2$ when using nitrogen as the dopant**

| Method | Dopant | Performance of modified photocatalyst                                                                 | References |
|--------|--------|------------------------------------------------------------------------------------------------------|------------|
| Sol gel | Nitrogen | • Anatase, rutile and titanium nitride phase were observed for N-TiO$_2$.  
• SEM analysis showed lamellar isolated aggregates.  
• Band gap of samples showed 3.123, 3.092, 3.054, and 3.009 which is lower | [14]       |
compare to pure TiO$_2$ (3.642 eV)

- Photocatalyst consist of anatase phase only.
- Band gap was narrowed compare to pure TiO$_2$.
- The morphology of N-TiO$_2$ showed in sphere.
- Band gap of N-TiO$_2$ showed 3.00, 2.96, and 2.92 eV which is lowed compared to pure TiO$_2$ (3.2 eV).

3. Magnesium as dopant

Avasalara et al., (2016) reported that magnesium doping with TiO$_2$ may synthesised a better photocatalyst and affect the dopant size on photocatalytic activity. Hence, magnesium is chosen as a dopant and photocatalytic activity on methyl orange (MO). XRD studies of Mg-TiO$_2$ by Avasalara, et al. (2016), showed that there is a formation of less dense antase phase which by means that the tight packing arrangement required for the formation of rutile phase is fully suppressed when magnesium nitrate has been added [19]. This is because the polarity of water has been enhanced and facilitated the formation of anatase phase exclusively. Titanium dioxide in the anatase form is claimed to be the most photoactive and practical of the semiconductor for the environmental application. MgO peaks were not observed from the XRD which indicated that Mg$^{+2}$ ion may be introduced into TiO$_2$ crystal lattice substitutionally. The UV-visible absorption spectra of Mg-TiO$_2$ has shifted to higher wavelength at 400-550 nm compare to the pure TiO$_2$ which indicated that the band gap has been reduced by magnesium doping. The morphological of Mg-TiO$_2$ showed irregular particle shape which was again aggregates of tiny crystal, while pure TiO$_2$ were observed to have large spherical with average particle size of 3.8 μm. This clearly suggested that the size and morphology of TiO$_2$ is altered when doped with magnesium. The photocatalytic activity also revealed that Mg-TiO$_2$ caused an enhancement than the pure TiO$_2$.

Another study for magnesium doped TiO$_2$ have been conducted by Devi and Panigrahi, (2015)[20]. In this research, the Mg-TiO$_2$ thin film was prepared by using the method of sol-gel and the optical properties was studied by UV Vis spectrophotometer within the wavelength of 300-900 nm. The absorption percentage of Mg-TiO$_2$ was higher compared to pure TiO$_2$ films which led the Mg-TiO$_2$ to become a visible light active of TiO$_2$ nano thin films. This has indicated that Mg doping enhanced the absorbance of TiO$_2$ thin film in the visible light range. The band gap of Mg-TiO$_2$ showed lower value compared to the pure TiO$_2$ which were 1.79 eV and 2.66 eV respectively.

Mg-TiO$_2$ nanoparticles synthesised by Behnajady et al. (2011)[4], proved the size and morphology of TiO$_2$ as influenced by magnesium doping from SEM analysis. SEM analysis showed that Mg-TiO$_2$ has smaller grain size and agglomerated to larger particle. XRD analysis showed all anatase phase for pure TiO$_2$ and Mg-TiO$_2$ at calcination temperature of 450 °C, while Mg-TiO$_2$ calcine at 650 °C consists of all rutile phase. The peak of Mg that is absent indicates the low metal ion dopant content as well as appropriate dispersion of metal ion deposit on TiO$_2$ nanoparticles. XRD data also showed that magnesium doping affected the high intensity and sharpened the anatase peaks where the crystallinity of anatase phase was enhanced too. The band gap for Mg-TiO$_2$ was calculated to be at 2.92 eV which was lower than pure TiO$_2$ and thus the photocatalytic activity is considered as efficient for Mg-TiO$_2$ with complete mineralisation of 99 % in 120 minutes radiation.

Sitthichai et al. (2017) conducted a research for magnesium doping ZnO by using sol-gel and analysed the structure of photocatalyst [21]. The XRD peaks of all samples showed strong and sharp peaks which indicating the high crystalline wurtzine ZnO sample with hexagonal structure. The crystallite size of Mg-ZnO was calculated by using the Scherrer equation and the average size of ZnO was 92 nm while for Mg-ZnO was 43 nm. The magnesium doping showed improvement in the
crystallites size, which mean, as the crystallite size is decreasing, the surface area is increasing too. Transmission electron microscopic (TEM) showed that the particle size decreased gradually when the Mg content is increasing. This is proved when the particle size was calculated using the XRD patterns. The efficiency of photocatalytic activity of Mg-ZnO and pure ZnO were evaluated and Mg-ZnO indicates high efficiency compared to the pure ZnO. The finding indicates that the ZnO structure, morphology and size has been improved when magnesium is incorporated into the ZnO structure. Also, highest efficiency of photocatalytic activity was found when Mg-ZnO was applied.

Shivaraju et al. (2017), has studied the degradation of industrial dyes using Mg-TiO$_2$ under the sunlight and found that the band gap energy shifted and exhibited a strong absorption band at 380-420 nm [22]. The Mg-TiO$_2$ also showed broad absorption edges at 398 nm which is in the range of visible spectrum of light compared to the pure TiO$_2$. The shift in the absorption edge to smaller photon energy indicates a decreased energy level in the conduction band thus the band gap energy is narrowed [23]. The XRD data showed that the mixed phases of anatase and rutile were observed because of the Mg dopant in the formation of TiO$_2$ crystals. Pure TiO$_2$ exhibits only pure anatase, while the spectrum of Mg-TiO$_2$ polyscales is different from TiO$_2$ which causes the broadening and decrease in the peak intensity. However, the Mg-TiO$_2$ has shown an increment in peak intensity which inducing well the crystalline phases, while proving that the photocatalyst as stable and photochemical activities could be enhanced [1] [24].

Next research on magnesium as dopant is investigated by Lefu and Kaiming (2010) where the photocatalyst were synthesised by using sol-gel method [25]. The XRD analysis has shown that only anatase phase is observed for pure TiO$_2$ and mixture of rutile and anatase is observed for Mg-doped TiO$_2$, both samples were annealed at 600 °C. The XRD peaks of Mg-TiO$_2$ appeared in sharp anatase and rutile phase has proved that the photocatalyst is stabilized by magnesium doping. The photodegradation rate of Mg-TiO$_2$ is evaluated at 75.2 % which is higher than pure TiO$_2$ with photodegradation rate of 47.3 %.

Prabu and Anbarasan (2014) have prepared and characterised the magnesium, silver and bismuth doped TiO$_2$ for solar cell applications by using acid modified sol-gel method [28]. The UV-Vis absorption spectroscopy showed that the modified TiO$_2$ have the strongest absorption within the wavelength in the range at 700-850 nm. The photo absorption of modified TiO$_2$ in the visible-light region was stronger than that of pure TiO$_2$. The band gap energy for the samples were 1.696, 1.538 and 1.481 for Ag-TiO$_2$, Mg-TiO$_2$ and Bi-TiO$_2$ respectively. The FESEM micrographs of the samples are observed uniform in size, clean and roughly spherical in shape. The crystallites agglomerated and fused together to form comparatively smaller irregular grains which will give higher porosity to the photocatalyst. Thus, the photovoltaic performance will be increasing. Meanwhile, the FESEM of pure TiO$_2$ showed larger and non-uniform distribution of spherical particles. Thus, from this research, the doping of magnesium, silver and bismuth can shift the band gap to the visible region and smaller crystallites will be formed, which will eventually enhance the photocatalytic activity.

**Table 3.** Summarized all the findings of using magnesium as the dopant

| Method | Dopant | Performance of modified photocatalyst | References |
|--------|--------|--------------------------------------|------------|
| Sol gel | Magnesium | • Mg-TiO$_2$ has smaller grain size and agglomerated compare to pure TiO$_2$.  
• Band gap of Mg-TiO$_2$ is 2.92 eV which is lower than pure TiO$_2$.  
• Photocatalytic efficiency was efficient with complete | [4] |
mineralisation of 99 % in 120 minutes irradiation.
- Mg-ZnO (43 nm) average size was smaller than ZnO (92 nm).
- The efficiency of photocatalytic activity of Mg-ZnO higher compare to ZnO.
- Mg-TiO2 exhibited a strong absorption band at 380-420 nm.
- Mixture of anatase and rutile were found in Mg-TiO2.
  - Band gap of MgTiO2 is 1.79 eV which is lower than pure TiO2 (2.66 eV).
  - Optical properties were within the wavelength of 300-900nm.
  - The absorption percentage of Mg-TiO2 was higher than pure TiO2.

Table 4. Method and performance of modified TiO2 when using metal as the dopant

| Method            | Dopant   | Performance of modified photocatalyst                                                                 | References |
|-------------------|----------|--------------------------------------------------------------------------------------------------------|------------|
| Sol gel           | Magnesium| • Both rutile and anatase were found in Mg-TiO2.                                                       | [25]       |
|                   |          | • Photodegradation of Mg-TiO2 is evaluated at 75.2 % while pure TiO2 only 47.3 %.                        |            |
| Acid modified sol | Magnesium| • UV-Vis absorption showed that modified TiO2 have the strongest absorption within the wavelength 700-850 nm. | [28][29]  |
| gel               | Bismuth  | • Band gap for Ag-TiO2, Mg-TiO2 and Bi-TiO2 were 1.696, 1.538 and 1.481 which lower than pure TiO2.       |            |
|                   | Silver   | • Samples were observed have uniform size, clean and roughly spherical in shape.                        |            |

4. Conclusion
Many treatment methods are available for the wastewater treatment, but suitable ways to remove the dyes and pigments altogether from the wastewater are still in the study. From this review study, nitrogen and magnesium shows as a capable dopant for photocatalysis process, especially in wastewater treatment.

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