Synthesis N doped TiO$_2$/PTFE by solvothermal method and their self-cleaning performance

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Abstract. Nitrogen doped TiO$_2$/PTFE with unique characteristic and photocatalytic self-cleaning activity under visible light were successfully produced using a modified solvothermal method with urea as the nitrogen source. This study combines photocatalyst of inorganic materials (TiO$_2$) with superhydrophobic polymers (PTFE) for self-cleaning glass coating. The X-Ray Diffraction show that the composite crystalline and new peak formed as indicated of PTFE. FTIR showed the presence of C-F groups on N doped TiO$_2$, which indicates that the composite material has been successfully formed. The morphology by scanning electron microscopy showed that agglomeration formed from N doped TiO$_2$/PTFE. The composite coatings showed a contact angle of 111.4°. The results confirm that the synthesized TiO$_2$ were successfully doped with nitrogen and composite with PTFE, allowing a higher photocatalytic activity. The composite N doped TiO$_2$/PTFE has completely coated on a glass substrate and enable to degrade methylene blue up to 79.9% for 1 hour irradiation.

1. Introduction

Recently, the use of glass that have transparent property used to in building, and as alternative save energy due to its benefits as room lighting any heating of building. The development of glass production process leads to a more widespread but there is a problem such as easy to be contaminated that will cause the reduction of lighting in a room and even can damage the surface materials. Various strategies have been developed to overcome these problems, one of them is through self-cleaning surface technology [1]. Titanium dioxide is one of extensive materials to be investigated, because has hydrophobic and hydrophilic. Titanium dioxide (TiO$_2$) is the best material for removal organic pollutant so can act as photocatalyst [2].

There are three crystalline phase in TiO$_2$ they are: anatase, rutile (the most stable), and brookite, where rutile and anatase phases show better photocatalytic reactivity. The rutile phase seems to low photocatalytic performances than anatase because anatase has a larger of area so it has a high active side [2]. The disadvantage of TiO$_2$ is the band gap in the large pure anastase structure, which showed 3.2 eV that makes this material only can be activated under high-energy UV light [3]. Expansion of the TiO$_2$ thin films can be done by shifting the absorption of light from the UV light region through doping with non-
metallic elements such as nitrogen [3]. Nitrogen can reduce the band gap and easily incorporated into the TiO$_2$ structure because its atomic size is proportional to oxygen, low ionization energy and high stability [4].

Enhancement the light absorption towards the visible range (longer wavelengths) and to improve the photocatalytic performances of TiO$_2$, many methodologies have been employed with: with organic dyes sensitization [5], deposition TiO$_2$ surface with metal ions [6], transition metals and non-metals (such as Nitrogen) doped [2]. Recent research reports that N is effective in narrowing the TiO$_2$ band gap, because N from 2p orbital can be intersection with 2p orbitals from O TiO$_2$. The electron in the valence band play an important role in the photocatalytic oxidation reaction, that because the holes in the valence band are used for the reaction [7]. Therefore N doping affects the catalytic activity and the ability of absorption of visible light.

On the other hand superhydrophilic photocatalytic materials has more disadvantages than superhydrophobic photocatalytic materials. The advantages of superhydrophobic materials application as self-cleaning surfaces, including the superior cleaning action of the lotus effect, in addition to providing other superhydrophobic properties such as water proofing [8]. However, there were a little examples in nature for superhydrophobic surfaces and minimum information for superhydrophobic photocatalytic surface act as photocatalysts [9]. Including fluorocarbon polymers such as polytetrafluoroethylene is one of organic materials with lower surface energy, were selected as hydrophobic agency [10].

Fluorocarbon polymer like polytetrafluoroethylene (PTFE), has been used in many field because it has high flexibility, heat and corrosion resistant [10]. Feng et al (2002) [11] report the use of alkyl fluoride as superhydrophobic material, alkyl fluoride like -CF$_2$H, -CF$_3$H and -CF$_3$ effective enough to reduce surface free energy. Polytetrafluoroethylene (PTFE) has the lowest surface energy materials known, with excellent resistance to chemical reagents, and has a high temperature stability. The surface of a PTFE plate has a static water CA of 108°, and a SA >90°, indicating water adhesion to the PTFE surface [12].

The present research aimed to synthesize Nitrogen doped TiO$_2$ by hydrothermal. Composite N-TiO$_2$/PTFE were prepare by solvothermal and coating on glass to extend the self-cleaning photocatalytic activity of TiO$_2$ into the visible light region, thus obtaining a better photocatalytic efficiency. The Nitrogen doped TiO$_2$/PTFE coatings on glass were test for the degradation of methylene blue to identification the self-cleaning photocatalytic performance.

2. Experimental

2.1 Materials

Titanium (IV) isopropoxide (Ti[OCH(CH$_3$)$_2$]$_4$) or TTIP was bought from Merck. Ethanol for analysis (≥99.99%) was purchased from Merck. Isopropyl alcohol was bought from Merck. Methylene blue as a dye was bought from Merck. Urea as nitrogen source. Ultrapure water was used all through the experiments.

2.2 Synthesis N doped TiO$_2$/PTFE

Synthesis of TiO$_2$ was carried out by the hydrothermal method. TTIP is added to isopropyl alcohol and distilled water in a ratio of 1:4. The mixture was added NH$_4$OH to pH 8 and keep stirrer for 2 hours. Then added urea and hydrothermal at 200 °C for 10 hours. Then, precipitates were washing with ethanol and distilled water for 3 times. After drying at 60 °C in oven, the white N doped TiO$_2$ was calcined at 600 °C for 1 hour. Polytetrafluoroethylene (PTFE) micropowders was dissolved in ethanol and mixed with N doped TiO$_2$ with ratio of 1:1 and stirrer for few hours. After that, the mixture were poured into autoclave. The autoclave was stirred and keep at 200 °C for 10h. After that, the white precipitates was drying in oven at 80 °C.

2.3 Photocatalytic self-cleaning experiment

The activities of the materials self-cleaning N doped TiO$_2$/PTFE were evaluated by photocatalytic degradation of Methylene blue. Methylene blue was added on the glass where coated with N doped TiO$_2$/
PTFE and then irradiated using a 300 watt halogen lamp as a photon energy source in a closed reactor with various irradiation time of 0-60 minutes with 5 minute increment.

2.4 Characterization
The X-ray diffraction (XRD) of each powdery TiO$_2$ was obtained with Cu Kα radiation ($\lambda = 1.5418$ Å) and characterized 2θ from 5-80°. The characterization by Scanning Electron microscopy (SEM) to observe morphology of samples. Fourier Transform Infrared (FT-IR) Spectroscopy to identification IR spectra. Degradation of methylene blue were determined by UV Vis Spectrophotometer.

3. Results and Discussion
The result of XRD characterization shows by Figure 1. Nitrogen doping affect the crystallinity of TiO$_2$. The results shows the suitability with JCPDS standart number 21-1272. The change of relative intensity peaks on diffractogram showed the difference amount and value of crystal field that measured. That because the arrangement of N structure on TiO$_2$. Each dominant peak showed on 2θ = 25.4° (101), 38.2° (004), 48° (200), 53.8° (105), 54.9° (211) that identified as anatase phase. It is showed that every diffraction peak was an anastase phase and does not appear brookite or rutile phase. The presence of nitrogen not form a new difractogram, that because a low of dopan consentration [13] and the dopan only affect the crystal lattice. The characteristic peaks of anatase TiO$_2$ shift to higher angles that confirm the dopan nitrogen cause shift of angles. The difference of N and O binding characteristics influence the shift of TiO$_2$ angles. The addition of PTFE causes new diffractogram on 2θ=18.1 ° according to Surmenenv et al., 2017 [14].

![Figure 1. XRD Pattern of TiO$_2$, N doped TiO$_2$, and N doped TiO$_2$/PTFE.](image)

FT-IR spectrum of TiO$_2$, nitrogen-doped TiO$_2$ samples with urea as nitrogen sources and N doped TiO$_2$/PTFE are shown in Figure 2. In 3434-1630 cm$^{-1}$ peak, identified as water and hydroxyl. Vibration of Ti-O-Ti bond were identification about 500 cm$^{-1}$. The peak N-H bending of nitrogen atoms substitute into TiO$_2$ identification at at 1440 cm$^{-1}$. Polytetrafluoroethylene groups identified on 512 cm$^{-1}$ peak, where on the peak occurred an overlapping between Ti and C-F.
Figure 2. Spectrum of Nitrogen-doped TiO$_2$, TiO$_2$/PTFE and N doped TiO$_2$/PTFE characterized by FTIR.

The morphology of nitrogen-doped TiO$_2$ sample are shown in Figure 3 with 2500x magnification. It was found that the as-synthesized TiO$_2$ shown of bulky and several hundred micrometers in length. It can be seen Nitrogen addition affects the morphological characteristics of TiO$_2$. Nitrogen can inhibit the growth of TiO$_2$. The composite of Nitrogen doped TiO$_2$/PTFE is agglomerate and not structured, because TiO$_2$ blend with polymer.

Figure 3. (a) Morphology of Nitrogen doped TiO$_2$ with 2500x magnification (b) Nitrogen doped TiO$_2$/PTFE with 300x magnification.

As seen in Figure 4 and 5, N doped TiO$_2$/PTFE-coated glass substrate is hydrophobic (111.4º) and glass substrate uncoating N doped TiO$_2$/PTFE high wettability (72.7º). To understand the characteristic of hydrophobic surface, the glass layer has been coated with material and the glass without coating drops of various liquids like coffee, rhodamin b, and methylene blue. The results did not show any differences to the hydrophobic properties from N doped TiO$_2$/PTFE coated on glass.
Figure 4. Repelling performance of different liquids on the substrat coating with N doped TiO$_2$/PTFE.

Figure 5. Repelling performance of different liquids on the substrat uncoating.

In real-life conditions, organic and inorganic particles will certainly contaminate surface coatings, hence the need for hidrophobic surfaces with self-cleaning properties. The advantages of hidrophopic surface is lower cost and effort consumption, because the surface can rapidly and effortlessly clean [10]. The photocatalytic self-cleaning properties of N doped TiO$_2$/PTFE coatings can demonstrate by ability of the film to degrade dye such as methylene blue.

The photocatalytic activity of modified materials was carried out with irradiation time variations of 0-60 minutes. Absorbance measurement is carried out at the maximum wavelength which can be used to obtain photodegradation. Methylene blue degradation results are shown in Figure 6 and Table 1. The methylene blue molecularly degraded because of the reaction with radical like O$_2$• and/or OH• which formed during the photochemistry reaction. The process begin when the energy hits the modification material, electron will be excited from valence band to conduction band (e$^-$) and leaves positive charge, hole (h$^+$) in the valence band. The excited electron will trapped on the modified-TiO$_2$ surface and some of them recombined then results heat. While the trapped excited electron undergo reaction with O$_2$ yielding O$_2$• and also react with H$_2$O then produce OH• [15]. Both radicals are detoxication agent that contribute to the methylene blue degradation.

The best percentage degradation of methylene blue aqueous solution by nitrogen doped TiO$_2$/PTFE at 79.9% with visible light irradiation for 1h, this shows that N doped TiO$_2$ which is composed with PTFE hydrophobic polymer has a good self-cleaning photocatalyst ability.
Figure 6. UV-Vis spectra of methylene blue under irradiation by N doped TiO$_2$/PTFE coating on glass substrate.

The existence of nitrogen is able to decrease the band gap energy so that it can suppress of recombination between electron-hole pairs produced. The irradiation time for $\Delta t/A_0$ show that the longer irradiation (1h) increase photodegradation of methylene blue because the longer irradiation, more electrons are excited, hole (h$^+$) that formed also increase so a radical amount hydroxyl which plays a role in the photodegradation process increases. The irradiation time for N doped TiO$_2$/PTFE photocatalysts for methylene blue degradation is shown in Figure 7. The photocatalytic optimization is obtained from the percent degradation shown in Table 1.

Figure 7. Photodegradation kinetic of methylene blue under visible light irradiation.
Table 1. Methylene blue degradation by N doped TiO<sub>2</sub>/PTFE and N doped TiO<sub>2</sub> composites on glass substrate

| composite variation | Percentage of Methylene blue degradation based on time variation (%) |
|---------------------|---------------------------------------------------------------|
|                     | 0     | 5     | 10    | 15    | 20    | 25    | 30    | 35    | 40    | 45    | 50    | 55    | 60    |
| N doped TiO<sub>2</sub>/PTFE | 27.1  | 25.3  | 28.7  | 31.7  | 45    | 45.7  | 53.3  | 65    | 71.4  | 73.6  | 74.6  | 79.9  |

4. Conclusion

Synthesis of Nitrogen-doped TiO<sub>2</sub> was successfully with hydrothermal method that combined with polymer PTFE by solvothermal method. After that, it was proved polytetrafluoroethylene groups identified on 512 cm<sup>-1</sup> peak by FT-IR analysis. The nitrogen atom embedded in TiO<sub>2</sub> indicated at 1440 cm<sup>-1</sup>. After nitrogen-doped and PTFE composite, the photocatalytic activity was greatly. The optimum percentage degradation of methylene blue by N doped TiO<sub>2</sub>/PTFE at 79.9% with visible light irradiation for 1h. The addition of nitrogen increases photocatalytic activity and PTFE increases the contact angle of self-cleaning glass.

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