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Research Article

Fabrication of photocatalyst film based on TEMPO-oxidized cellulose nanofiber

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Keywords

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Abstract

The powerful performance of TiO_2 and its doped as photocatalyst material initiated the finding of new technique that efficient and effective to degrade the organic pollutant, i.e., azo dyes. This study examined photocatalyst film's photoactivity, TEMPO-oxidized cellulose-containing N-TiO_2 (TOC/N-TiO_2), on the degradation of azo dyes. TEMPO-oxidized cellulose, which has a negative charge, was sequentially mixed and stirred in the suspension of TiO_2 and doped TiO_2. This experiment utilized several instruments to determine the physicochemical properties of the photocatalyst film. The UV-DRS and diffractogram data confirmed the anatase phase as the only phase found in N-TiO_2, which has a lower bandgap value than the anatase TiO_2. These data demonstrated the superior photocatalytic of TOC/ N-TiO_2 against azo dyes.

Introduction

As a natural polymer, cellulose has attracted much attention due to its excellent and promising properties, e.g., mechanical properties, flexibility, biocompatibility, etc. (Mahendra et al. 2019a). Another reason cellulose becomes popular is the easy process of performing physical and or chemical functionalization on its surfaces, either with organic or inorganic material (Ezati et al. 2019; Vatansever et al. 2019).

TEMPO-oxidized cellulose nanofiber (TOC) is the immensely popular derivate of cellulose with superior properties due to high transparency, high L/D ratio. The inorganic material, i.e., metals, metal oxides, semiconductors, etc. (Henry et al. 2015; Kale et al. 2016; El-Gendy et al. 2017), can enhance the performance of TOC for a wide range of applications. Among the popular semiconductor materials, incorporating TiO_2 into the TOC matrix can be used for developing photocatalyst film as an alternative to reduce the organic contaminant in water environments.

Modification of TiO_2 through the doping process could enhance its photocatalytic and able to work under visible light (Nolan et al. 2012; Mathews et al. 2015; Aware and Jadhav 2016; Mahendra et al. 2019b). The previous studies already covered cellulose's functionalization using TiO_2 or doped-TiO_2. However, most studies focus on the fabricating composite in granule form or only using pristine cellulose to fabricate a film composite (Morawski et al. 2013; Chen et al. 2017; Al-Ahmed et al. 2019; Arularasu et al. 2020). Those previous studies utilized several chemicals to produce soluble cellulose that was ineffective, inefficient, and not environmentally friendly.

Here we over a novel photocatalyst film constructed by TOC and N-TiO_2. The objective of this study is to evaluate the performance of TOC/doped TiO_2 as photocatalyst film for the dyes degradation in comparison to TOC/undoped TiO_2. The use of TOC in this study is relatively environmentally friendly, and we minimized the utilization of organic solvent for obtaining a soluble form of cellulose. In this study, we used a high-pressure homogenizer to get a gel-like form of cellulose nanofiber. The as-prepared photocatalyst film offered promising activities as photocatalyst materials.

Method

This research was performed in three stages, i.e., preparation of TOC, preparation of doped TiO_2, and preparation of TOC/doped TiO_2.

Materials

The empty fruit bunches oil palm was obtained from oil palm plantation in Riau, Indonesia. TEMPO, sodium hypochlorite, sodium bromide, sodium hydroxide, ethanol, titanium isopropoxide were purchased from Sigma Aldrich. All chemical above was used directly without any further treatment.

Preparation of TEMPO-oxidized Cellulose Nanofiber (TOC)

The TOC was prepared by following a method from our previous study (Mahendra et al. 2019a). The lignin and hemicellulose were partially removed through a bleaching process using NaOCl and H_2O_2. Combined with mechanical treatment, the fiber then oxidized using TEMPO/NaBr/NaOCl at pH 10 for six hours. The fibrillation of fiber then performed using a high-pressure homogenizer (GEA PandaPlus 2000) for six cycles at 600 bar.

Preparation of N-TiO_2

Nitrogen doped TiO_2 was prepared using sol-gel technique that assisted by hydrothermal technique (Mahendra et al. 2019b). The precursor was titanium isopropoxide. The mentioned technique was successfully developed a robust photoactive material from TiO_2 precursor.

Preparation of TOC/ N-TiO_2 film

The as-prepared TOC with consistency 1.0 wt.% was cut using blend knives and homogenized using Ultra Turax. The photocatalyst film of TOC/N-TiO_2 was prepared in 2:1 of mass ratio. The photocatalyst film of TOC/N-TiO_2 was then transferred into Teflon surface and dried in a vacuum oven at 60°C. The photocatalytic performance was performed by following the previous studies (Huda et al. 2019; Mahendra et al. 2019b).

Results and Discussion

Fig.-1(a) shows the morphological of the lyophilized TOC/N-TiO_2 composite. The aggregate of N-TiO_2 appears on the surface of TOC. This result is quite similar to the N-TiO_2 in the previous studies (Al-Ahmed et al. 2019; Mahendra et al. 2019b; Arularasu et al. 2020).

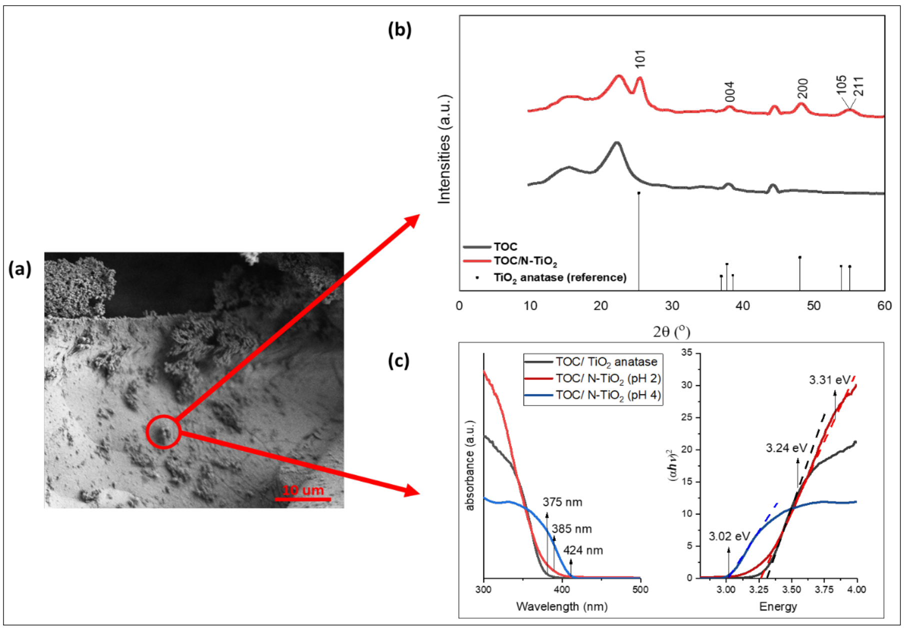

Fig.-1. (a) Morphological of TOC/N-TiO_2, (b) Diffractogram of TOC/N-TiO_2, and (c) UV-Vis/DRS Spectra of TOC/N-TiO_2.

Fig.-1(b) shows the diffractogram of the as-prepared photocatalyst film TOC/N-TiO_2. It confirms the TOC matrix showed cellulose type I characteristic through signals at 2θ of 16.5, 22.5, and 34.5° (Chen et al. 2017; Rohaizu and Wanrosli 2017; Mahendra et al. 2019a). After incorporating N-TiO_2 into the TOC matrix, several new signals appeared at 25.1, 48.0, and 53.5°. These new signals confirmed the anatase phase's presence on the as-prepared N-TiO_2 (Wang et al. 2016; Fischer et al. 2017; Mahendra et al. 2019b). Fig.-1(c) shows the UV-Vis diffuse reflectance spectra, and it demonstrates that the as-prepared N-TiO_2 at pH 2 and pH 4 have visible-light response. Incorporating N-TiO_2 prepared at pH 4 into the TOC matrix showed the highest photoresponse at the visible light range. The additional data from UV-Vis DRS is about the bandgap energy of each material. The photocatalyst film of TOC/N-TiO_2 pH 4 (3.02 eV) shows the lowest bandgap energy compared to TOC/N-TiO_2 pH 2 (3.24 eV) and TiO_2 anatase (3.31 eV). The decrease of bandgap energy value indicated that nitrogen's doping process into the titania lattice was successfully performed (Wang et al. 2010; Mekprasart and Pecharapa 2011; Nolan et al. 2012; Ramchiary and Samdarshi 2015; Chen et al. 2017). Another possibility is that the as-prepared material will have lower crystallite size at a low pH, affecting the increase of bandgap energy value of materials (Tsega and Dejene, 2017).

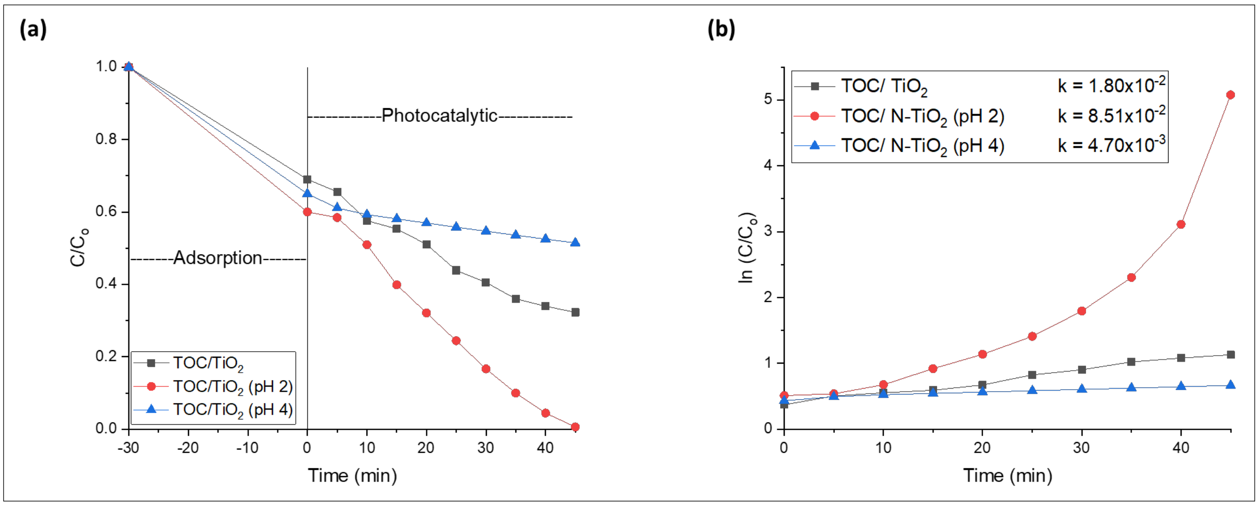

Fig.-2. Photocatalytic of TOC/N-TiO_2 Against Direct Blue 71 (DB71).

The photocatalytic study was initiated by conducting the adsorption and desorption behavior of the photocatalyst film. The result showed that the removal/ absorption percentage of DB71 was about 30-40%. This high adsorption capacity is due to the TOC matrix's high surface area (Nolan et al. 2012; Al-Ahmed et al. 2019). The high adsorption also could be influenced due to the presence of the positive charge in DB71 structure that can interact through electrostatic interaction with the negative charge of TOC from the carboxylic group. In Fig.-2(a), the photocatalyst film's removal dyes capability is relatively high, and the photocatalyst film in the presence of doped TiO_2 showed superior activity than the photocatalyst film in the presence of pristine TiO_2. After 45 min treating with UV irradiation, TOC/N-TiO_2 pH 2 showed 99.95% of dyes removal, followed by TOC/TiO_2 and TOC/N-TiO_2 pH 4 with the dye removal percentage of ~68 and ~49%, respectively. The adsorption process plays a significant role during the dye removal, and based on this result, there is a synergy activity between the adsorption and photocatalytic on the TOC/N-TiO_2 surface, which brings a positive result on the dye removal. The photocatalytic performances of TOC/N-TiO_2 (pH 4) show the lowest activity, although it has the lowest bandgap energy value. Based on the diffractogram data, the N-TiO_2 (pH 4) is dominated by the rutile phase (80%) and followed by anatase (20%). As we all know, the TiO_2 rutile phase has the lowest performance among the TiO_2 phases.

Conclusion

The N-TiO_2 prepared at pH 2, and 4 was introduced into the TEMPO-oxidized cellulose nanofiber (TOC) gel-like form. The obtained TOC/N-TiO_2 photocatalyst film exhibited lower bandgap energy than the photocatalyst film contained pristine TiO_2. The photocatalyst N-TiO_2 showed superior activity in removing DB71, especially N-TiO_2 (pH 2)—the highest photoactivity of photocatalyst film (N-TiO_2 pH 2) due to the presence of anatase. Significantly different from the photocatalyst film N-TiO_2 (pH 4), which consisted of 80% of rutile and 20% of anatase, affect this material's photocatalytic performance with the lowest score.

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Conflict of Interests

Authors declare there are no conflicts, including any financial and non-financial interest.

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