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Degradation of air pollutants from waste burning using photocatalyst TiO_2 With $Co(NO_3)_2$ doped under ultraviolet irradiation

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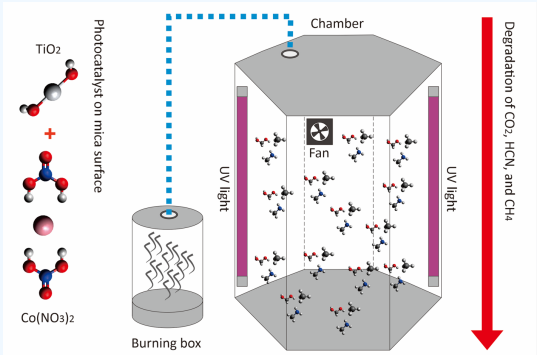
ABSTRACT

Air pollutants, such as carbon dioxide (CO_2), hydrogen cyanide (HCN), and methane (CH_4), can harm the respiratory organs of humans and cause several diseases. This study successfully utilized a photocatalyst from TiO_2 with $Co(NO_3)$ doped to degrade these air pollutants from waste burning. The photocatalyst layer was produced by dissolving TiO_2 and $Co(NO_3)_2$ in distilled water, and then the solution was coated on a mica surface using a spray coating method. The coated mica was then dried in an oven. The crystallite structure of $TiO_2/Co(NO_3)_2$ was analyzed by X-ray diffraction. The obtained crystallite size was (15.38 ± 0.03) nm with lattice parameters a and c were (3.8 ± 0.3) Å and (9.3 ± 0.3) Å, respectively, which shows that it is an anatase phase. The band gap energy was measured by diffuse reflectance UV-visible spectroscopy and analyzed using Tauc's plot method. The measured band gap energy of the photocatalyst was 2.81 eV, which can be easily activated by ultraviolet (UV) light. The photocatalyst sheets successfully degraded air pollutants from waste burning, including 53.139% CO_2 for 4 hours, 100% HCN for 10 minutes, and 72.381% CH_4 for 40 minutes. Therefore, the fabricated photocatalyst in this study can potentially be an alternative to degrading air pollutants, especially CO_2, HCN, and CH_4.



Keywords: *Photocatalyst, TiO_2, $Co(NO_3)_2$, Air Pollutants, UV Light*

1. INTRODUCTION

Fresh air is a very important element for living things. However, the fresh air issue has recently taken center stage because of air pollution. Air pollution is a mixture of gases and particles produced by many sources, such as the smoke of cigarettes, vehicles, industry, agriculture, combustion, and natural sources [1, 2, 3]. Several gases widely known as air pollutants include SO_2, NOx, NH_3, and CO, as well as greenhouse gases such as CO_2, CH_4, and N_2O [4, 5]. These pollutants pose significant risks to human health, particularly when they infiltrate indoor spaces through air vents. Confined within walls and roofs, these gases are impeded from dispersing naturally with the wind. Consequently, occupants inhale the pollution readily, leading to many health issues and compromising the overall comfort of the indoor environment [6].

Researchers have made various efforts to reduce air pollutants. Photocatalysis, an environmentally friendly and sustainable technique, holds great promise for degrading these pollutants [7, 8, 9]. Photocatalyst is a catalytic process whose success depends on light absorption capability, active site density, redox capacity, and the rate of light-triggered electron-hole recombination [10]. Titanium dioxide (TiO_2) is one of the most excellent and popular semiconductor photocatalysts, with good photosensitivity and chemical stability, non-toxicity, and low cost [11, 12]. TiO_2 has a crystallite size of 19.82 nm [13]. This crystal is divided into three polymorphic forms: rutile, anatase, and brookite [14, 15]. TiO_2 is used exclusively as a white pigment and has been widely used as a base material for producing sunscreen, photocatalysts, and solar cells [16]. However, this photocatalyst has limited optical and electronic properties that are active only when exposed to UV light [17], which is only ± 5% of solar energy [18]. The band gap energy on TiO_2 is about 3.23 eV [19].

Modifying the surface of TiO_2 by incorporating other materials is recognized as an effective technique to enhance the efficiency of sunlight utilization and broaden its photocatalytic activity [13]. Doping of metal ions (such as Fe, Co, Ag, Ni) and non-metallic elements (such as C, N, F, S) or carbon-containing materials (such as carbon nanotubes, flora, and graphene oxide) can improve the photocatalytic properties of TiO_2 [13, 17]. Among these materials, Co can effectively enhance the photocatalytic activity of TiO_2 [20]. When Co is introduced into the TiO_2 material, it acts as an impurity within the conduction band, leading to an electronic transition, namely the band gap transition from the valence band consisting of O 2p orbitals to the Co 3d and Ti 3d conduction bands. This intensity indicates that TiO_2/Co has good photocatalytic activity. After electron excitation, the pho-

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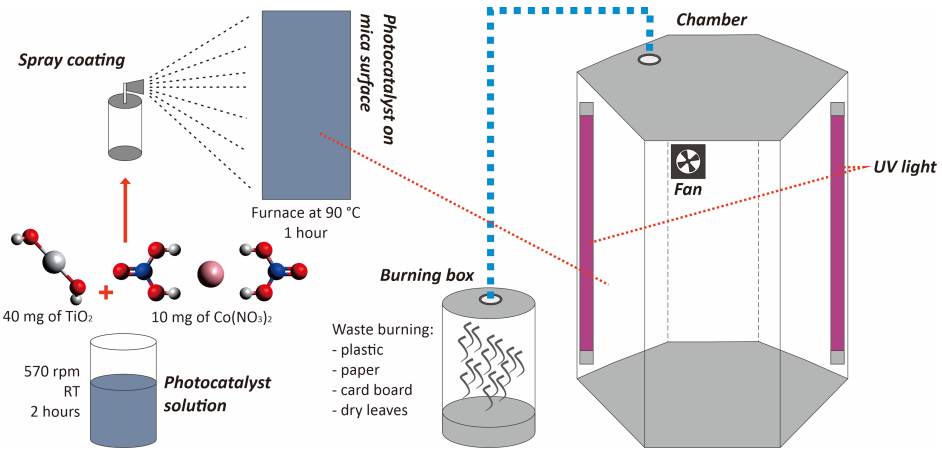

Figure 1. The chamber of photocatalyst test. The smoke sample flows from the burning box to the chamber. UV lamps are used as light sources.

togenerated electrons are reserved in the conduction band, which are further transferred to the surface of catalyst particles to be captured by O_2 molecules adsorbed on the surface. The photogenerated holes in the valence band are trapped by hydroxyl molecules and water as active radicals to oxidize organic compounds [20].

Hosseini et al. found that a fabricated photocatalytic mixed matrix membrane containing Co and TiO_2 nanoparticles was suitable for the photocatalytic separation of 2,4-dichlorophenol [13]. Khaki et al. also researched Co and TiO_2, which resulted in the bandgap energy of the transition metal Co-doped with TiO_2 being lower than that of TiO_2, which is 2.96 eV [17]. In addition to its utilization in liquid samples, TiO_2 can also be used in gas samples. Mamaghani et al. carried out hydrothermal/solvothermal synthesis and processing of TiO_2 as an effective photocatalyst for the degradation of air pollutants [21]. Therefore, research on photocatalysts for the degradation of air pollutants is possible.

In this study, TiO_2 with a Co-doped photocatalyst was fabricated. To assess the impact of Co doping on the crystallite structure of TiO_2, X-ray diffraction (XRD) patterns were conducted. Additionally, to confirm that Co doping reduces the band gap energy of TiO_2, testing was performed using diffuse reflection UV-visible (DR UV-Vis) spectroscopy. The photocatalyst was tested to degrade the air pollutants, namely CO_2, HCN, and CH_4, from waste burning under UV light irradiation. Gas concentrations were detected by a gas chromatography thermal conductivity detector (GC-TCD) and gas chromatography-mass spectroscopy (GC-MS).

2. MATERIAL AND METHODS

2.1 Materials and Instruments

The titanium dioxide (TiO_2) (anatase-type) powder is produced by Sigma Aldrich. Cobalt nitrate powder ($Co(NO_3)_2$) was purchased from Nitra Kimia, Indonesia. UV lamp (220V, 50 Hz, 6W) was used as light sources. X-ray diffraction (Shimadzu XRD-6000) and diffuse reflectance UV-visible spectroscopy (Shimadzu UV-1700) were used to characterize the photocatalyst doped. Contaminated smoke is generated from burned waste such as plastic, paper, cardboard, and dry leaves. The 5-mL venoject tube was used to collect the smoke samples. Gas chromatography thermal conductivity detector (GC-TCD, Shimadzu GC 8A) and gas chromatography-mass spectroscopy (GC-MS, Shimadzu QP 2010 SE) were utilized to measure the concentration of the molecules of the samples.

2.2 Method and Procedure

The testing chamber in this study was constructed using a modified hexagonal prismatic glass container with a hole for smoke and a hole for sample collection. UV lamps were installed inside the chamber as UV light sources. A fan was installed in one of the holes to introduce smoke so that the smoke would be attracted and enter the chamber. An illustration of the photocatalyst fabrication process and the test chamber are shown in Fig. 1. In this study, the TiO_2 photocatalyst was doped with Co derived from $Co(NO_3)_2$. 40 mg of TiO_2 and 10 mg of $Co(NO_3)_2$ were dissolved in 5 mL of distilled water and stirred with a stirring speed of 570 rpm for 2 hours at room temperature to produce a homogenous photocatalyst solution. The solution was then sprayed on two sheets of mica (13 × 29 cm) coated with aluminum foil for photocatalyst test under UV light. These sheets aim to cover the glass in the test room so that UV light does not radiate out. After spraying on the mica, the solution was dried in a furnace at 90 C for 1 hour. Then, the mica was mounted on the inner side of the test chamber.

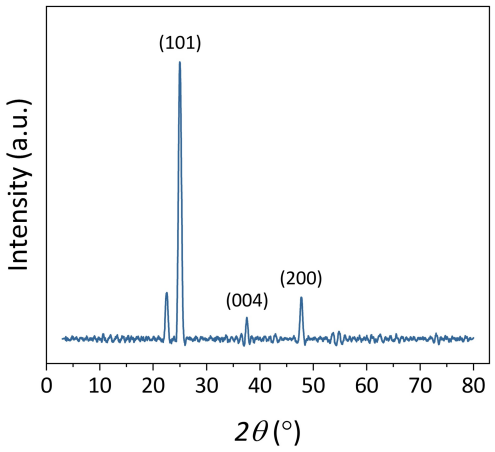

Figure 2. XRD pattern of $TiO_2/Co(NO_3)_2$ photocatalyst

The photocatalyst was synthesized in solid phase (powder) for material characterization and then tested using XRD

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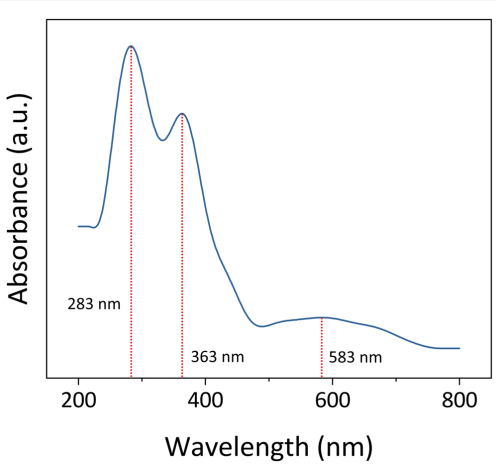

Figure 3. Absorbance spectrum of $TiO_2/Co(NO_3)_2$

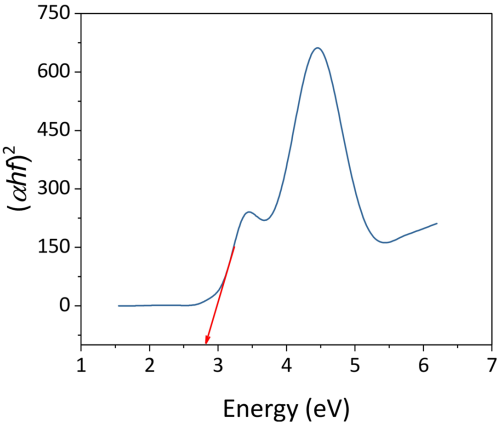

Figure 4. Tauc's plot on $TiO_2/Co(NO_3)_2$

to determine the type of crystal. Analysis was carried out with diffraction angles (2q) in the range of 3 C–80 C and scanned continuously at a scan rate of 4 degrees·s ^{1}. XRD was conditioned at a voltage of 40 kV with a current of 30 mA. The resulting data are 2q and intensity, then presented in a graph to determine the intensity peaks. The values calculated in XRD are crystallite size (t) and lattice parameters (a and c) with the following equations (Eq. 1 and Eq. 2).

$$t = \frac{K\,l}{b\cos q} \tag{1}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{2}$$

where K is Scherrer constant (0.9), l is X-ray wavelength (0.154 nm), b is the full width at half the maximum intensity of the reflection peak, q is diffraction angle, d is the distance between Bragg planes, and (hkl) is miller index [16]. Photocatalysts synthesized in the solid phase (powder) are also tested using DR UV-vis spectroscopy to ensure photocatalyst band gap energy changes after doping with $Co(NO_3)_2$. Data acquisition is performed at a wavelength of 200–800 nm every 1 nm. The data results were then analyzed using Tauc's Plot method, which is the relationship between absorption coefficient (a) and incident photon energy hf in the form of (Eq. 3):

$$(ahf)^{\frac{1}{m}} = c(hf \quad E_g) \tag{3}$$

where a is the absorbance coefficient used in the Tauc Plot method, h is the photon energy (eV), c is a constant, and Eg is the band gap energy. The value of m depends on the type of transition: m = 1/2 for direct and permitted transitions, m = 2 for indirect transitions, and m = 3/2 for forbidden transitions [22]. OriginLab software was used to determine the bandgap energy of the photocatalyst.

The photocatalyst test begins by filling the chamber to the brim with polluted smoke/gas by capturing the combustion exhaust using a funnel and hose connected to the vent hole in the chamber. The UV lamp is then turned on. Gas samples were taken with a syringe directly into a 5 mL venoject tube to preserve the gas. In the first test to observe the degradation of CO_2, samples were taken every 2 hours from before the reaction occurred (t = 0 s) to 6 hours. In the second test to observe the degradation of HCN and CH_4, samples were collected every 10 minutes from pre-reaction (t = 0 s) to 40 minutes.

Gas samples stored in venoject tubes were analyzed by GC-TCD and GC-MS to determine changes in the CO_2, HCN, and CH_4 concentrations after the photocatalyst test. The concentration of the molecules in the gas is indicated by the percentage of the area of the peaks on the graph produced by the detector. The percentage of CH_4 and CO_2 degradation is calculated using the following equation (see Eq. 4).

$$\text{Degradation}(\%) = \left(1 \quad \frac{C_t}{C_0}\right) \quad 100\% \tag{4}$$

where Ct is the concentration of the molecule at time t, and C_0 is the initial concentration of the molecule [13]

3. RESULTS AND DISCUSSION

3.1 Crystral Size Analysis of $TiO_2/Co(NO_3)_2$ Photocatalyst

The crystal structure of the photocatalyst layer used in this study was analyzed using an X-ray diffractometer (XDR). The data obtained was further analyzed using OriginLab software to determine the diffraction peaks. The peaks are the scattering of light hitting the TiO_2/Co crystal, which interferes constructively. The XRD patterns of $TiO_2/Co(NO_3)_2$ photocatalyst is shown in Fig 2.

Based on Fig. 2, diffraction peaks indicate that X-rays hit the crystal plane. Four diffraction peaks are visible on the $TiO_2/Co(NO_3)_2$, namely at 2q of 22.526 C, 25.013 C, 37.552 C, and 47.761 C. These diffraction peaks were compared with the TiO_2 standard diffractogram from the Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data (JCPDS-ICDD) No. 21–1272. The first peak did not find its Miller index from these data, so further analysis could not be performed. Meanwhile, the Miller indices at 2q of 25.013 C, 37.552 C, and 47.761 C are (101), (004), and (200), respectively. The results of this crystal field analysis indicate that the detected material is anatase-type TiO_2 [14, 15, 19]. The highest diffraction peak of the $TiO_2/Co(NO_3)_2$ photocatalyst is located at 2q of 25.013 C with plane (101). The peak appears due to the effect of the addition of $Co(NO_3)_2$ on TiO_2, which then characterizes the material we produce. Through the calculations in Eq. 1 and Eq. 2, the values in Table 1 are obtained.

Based on the calculations performed, the crystallite size of the $TiO_2/Co(NO_3)_2$ is (15.38 ± 0.03) nm. The crystallite size is smaller than pure TiO_2, which is 19.82 nm [13]. Co

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