Short Communication:

Doping TiO_2 with Cr and Cu Elements from Electroplating Wastewater as a Single Source for Improvement of the Photocatalyst Activity under Visible Light in the Degradation of Anionic Surfactant

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Received: February 6, 2024
Accepted: March 29, 2024

DOI: 10.22146/ijc.93928

Abstract: *This paper discusses the use of electroplating wastewater containing Cr and Cu as a single dopant source to improve the activity of TiO_2 photocatalysts under visible light. Sol-gel doping was used to dop TiO_2 with Cr and Cu in the wastewater. The doped TiO_2 photocatalysts were characterized using SRUV/visible and XRD instruments, and their effect on the degradation of linear alkyl benzene sulphonate (LAS) in laundry wastewater was evaluated. The electroplating wastewater used in this research contains Cr and Cu about 2000 and 20 mg/L, respectively. These metals were successfully doped into a TiO_2 structure, which significantly reduced the gap energy of TiO_2, allowing it to be more active under visible light. The highest photodegradation of the 125 mg/L LAS in 25 mL of the laundry wastewater with pH 7 was achieved by using 30 mg of TiO_2/Cr-Cu (200/2) photocatalyst, which degraded up to 60% of LAS in 60 min. With the same conditions, the LAS photodegradation increased to 100% upon the second run. This approach can help turn hazardous electroplating wastewater into a valuable material to solve environmental problems.*

Keywords: *electroplating wastewater; Cr-Cu; TiO_2; linear alkyl benzene sulphonate; photodegradation*

■ INTRODUCTION

Titanium dioxide (TiO_2) is an extensively researched photocatalyst for solving environmental issues due to its high activity, good stability against biological and chemical effects, cost-effectiveness, and non-toxicity [1-15]. Accordingly, TiO_2 has garnered significant attention and is frequently utilized in degrading various organic pollutants [1-4]. Unfortunately, with the large gap represented by band gap energy (E_g) as much as 3.2 eV, TiO_2 can only be activated with ultraviolet (UV) light or almost inactive under visible light and sunlight [14,16], striking it to be applied under cheap sunlight. This limitation is caused by the fact that UV light is present in only about 5% of sunlight [17], while visible light is found dominantly at about 65% [6-7].

Hence, it is clear that the extension of the TiO_2 application by improving its activity under visible light and sunlight is essential. Increasing TiO_2 activity under visible light has been intensively conducted by doping TiO_2 both with single [5-9] and two different metals [10-14]. Among metals, Cr [6-7,18] and Cu [8-9,19-20] elements are the favored dopants due to their considerable effect in improving TiO_2 activity under visible light. Introducing Cr or Cu dopants in TiO_2 structure can enable the trapping of electrons, leading to a decrease in the recombination rate of electron-hole pairs [21]. It makes the TiO_2 photocatalyst process more efficient. Cr dopants can reduce the E_g from 3.24 to 2.80 eV [22], while Cu doping can lower the E_g from 3.20

to 2.91 eV [13,23]. Furthermore, it is also notable that doping with double different metals showed more significant enhancement in the visible light-responsive TiO_2 photocatalyst compared to the respective single one [10-14]. The double metals that have been doped into TiO_2, include Cu and Cr with Mn [10], Cr with Ni [11], Cr with Fe [12], as well the combinations of Cu with Fe [13] and Cu with Ag [15].

In doping TiO_2 with Cr and Cu as single, as well as dual dopants, the related expensive commercial materials are frequently used [5-14] leading to less effective-cost doping. Accordingly, finding a cheaper dopant source, such as from associated wastewater [9,24] will be beneficial. Under the circumstances, in this present research, we propose electroplating wastewater containing high concentrations of Cr(VI) and Cu(II) ions as a cheaper single source of double dopants into TiO_2 photocatalyst.

It has been reported that electroplating wastewater contains noticeable concentrations of Cr and Cu ions [15], categorized into hazardous heavy metals [25]. The presence of two heavy hazardous metals in the environment can create ecosystem damage and human health problems [15,25]. It is believed, hence that the utilization of electroplating wastewater as a dopant source can prevent environmental pollution and, at the same time, can convert the harmful wastewater into valuable materials. So far, the utilization of the electroplating wastewater as a source for Cr and Cu dopants is not traceable, indicating this research's novelty.

The effect of the doping with double dopant on the enhanced TiO_2 activity under visible light in this paper is evaluated through the degradation of linear alkyl benzene sulphonate (LAS) in real laundry wastewater. LAS is an anionic detergent and is the most widely used surfactant in the world [26-27]. In accordance, a very large volume of laundry wastewater with high LAS concentration is routinely disposed of [26], causing accumulation in the environment. LAS has been reported to cause hepatotoxicity in fish [27] and increase the growth rate of colon cancer cells, raising thereby its tumor promotion effect potential [26]. Therefore, it is urgent to reduce the LAS concentration in the laundry wastewater before reaching the ecosystem. To decrease LAS concentration in such wastewater, photocatalytic degradation over TiO_2 [28-30] and the doped TiO_2 [23] have been applied successfully. However, LAS removal from real laundry wastewater through a photodegradation mechanism in the presence of Cr-Cu doped TiO_2 under visible light has not been explored. In this present report, the best condition for photodegradation of LAS in real laundry wastewater has been afforded by optimizing the amount of the double dopants in TiO_2, photocatalyst mass, solution pH, and the irradiation time.

■ EXPERIMENTAL SECTION

Materials

Anatase-typed TiO_2, $Cu(NO_3)_2$, K_2CrO_4, and dodecyl alkyl benzene sulphonate (DBS) were purchased from Merck in pro analysis grade and used as received. The electroplating wastewater was taken from a metal plating company, and the laundry wastewater was taken from a laundry service located in Yogyakarta City, Indonesia.

Instrumentation

Doping TiO_2 was performed using Pyrex laboratory glassware and a magnetic stirrer Thermo Scientific Cimarec. Electroplating wastewater was analyzed using an atomic absorption spectrophotometer (AAS) Perkin Elmer 3110 and a UV-visible spectrophotometer, Thermo Scientific Orion Aqua Mate 8100. TiO_2/Cr-Cu photocatalysts were characterized by specular reflectance accessory of UV-1800 series (SRUV) Pharmaspec-1700 and X-ray diffraction (XRD) Shimadzu-6000.

Procedure

Analysis of the electroplating wastewater

The analysis was performed by visible spectrophotometry method to determine the concentrations of Cr(VI) ions by using diphenyl carbazide as a complexing agent and by atomic absorption spectrophotometry for determining Cu(II) ions concentration. Cr(VI) and Cu(II) concentrations were measured as ≈2000 mg/L and ≈20 mg/L, respectively.

Doping TiO_2 with Cr-Cu from electroplating wastewater

TiO_2 powder, weighed 1.0 g, suspended in water was mixed with 50 mL of the electroplating wastewater containing 2000 mg/L of Cr(VI) and 20 mg/L of Cu(II). Then, the mixture was stirred magnetically for 10 min to obtain a homogeneous mixture. Next, the homogeneous mixture was placed in the autoclave and was heated at 150 °C for 24 h. The doped photocatalyst in the autoclave was separated from the water and then dried at 90 °C for 2 h. The amount of Cr(VI) and Cu(II) doped was 100 and 1 mg/g TiO_2.

The same procedure was repeated for the electroplating wastewater with 100 and 150 mL of the volumes, which gave different concentrations of Cr (VI) and Cu(II) doped. By introducing the wastewater as much as 100 mL, the amount of Cr(VI) and Cu(II) doped were 200 and 2 mg, respectively. By reacting the wastewater with as much as 150 mL, the amount of Cr(VI) and Cu(II) doped were 300 and 3 mg, respectively for each 1 g of TiO_2. Thereby the three doped photocatalysts that have been prepared were noted as TiO_2/Cr(100)-Cu(1), TiO_2/Cr(200)-Cu(2), and TiO_2/Cr(300)-Cu(3).

Characterization

TiO_2/Cr-Cu photocatalysts were characterized by using SRUV and XRD. The sample's absorption edge and E_g were determined based on the SRUV spectra that were taken from 300 to 800 nm of the wavelength. The XRD patterns were measured from 4 to 40° of the 2θ angles with Cu-Kα radiation.

Photocatalytic degradation of LAS in laundry wastewater

TiO_2/Cr-Cu, as weighed 30 mg, was mixed with 25 mL of laundry wastewater containing 125 mg/L of LAS, and stirred constantly to mix well. The mixture was irradiated with a visible lamp and magnetically stirred for 60 min. Then, the mixture was centrifuged at 4000 rpm for 25 min to separate the solid from the filtrate. The determination of LAS concentration in the filtrate from the photodegradation process was carried out by using a UV-visible spectrophotometer based on the reaction with methylene blue, followed by extraction with chloroform. The amount of the LAS degraded (in %) was calculated by Eq. (1);

$$\%\text{Degradation} = \frac{C_0 - C_f}{C_0} \times 100\% \qquad (1)$$

where C_0 is the initial amount of LAS (mg/L), and C_f represents the amount left in the solution (mg/L). The same procedure also proceeded with various amounts of Cr-Cu doped in TiO_2 (Cr(100)-Cu(1), Cr(200)-Cu(2), Cr(300)-Cu(3)), photocatalyst masses (10, 20, 30, and 50 mg), pH (1, 3, 5, 7, 9, and, 12), and irradiation time (10, 20, 30, 45, 60, 75, and 90 min).

■ RESULTS AND DISCUSSION

Characterization Data

SR-UV/visible data

The spectra of SR-UV/visible of the undoped and the doped TiO_2 photocatalysts are displayed in Fig. 1. The spectra are used to determine the wavelength of the absorption edge and further the E_g of TiO_2. The absorption edge wavelength is determined by intersecting the straight lines of the wavelength and the absorbance. The wavelengths (λ) of the intersection obtained are presented in Table 1, along with the E_g values calculated based on the Tauc plot method, as seen in Fig. 2.

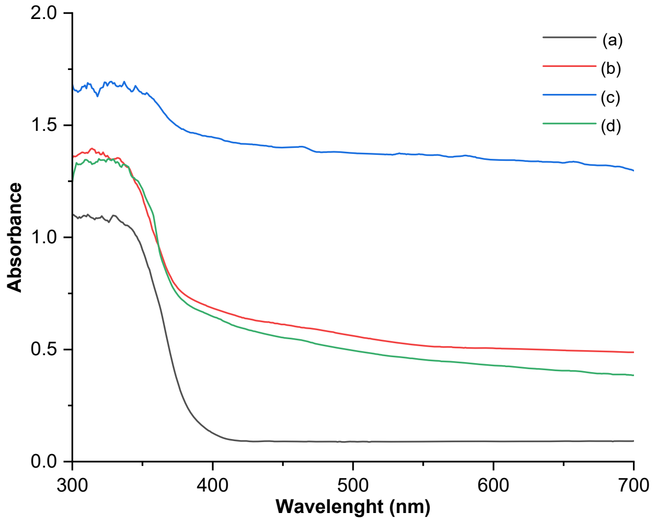

Fig 1. SR UV/visible spectra of (a) TiO_2, (b) TiO_2/Cr(100)-Cu(1), (c) TiO_2/Cr(200)-Cu(2), and (d) TiO_2/Cr(300)-Cu(3)

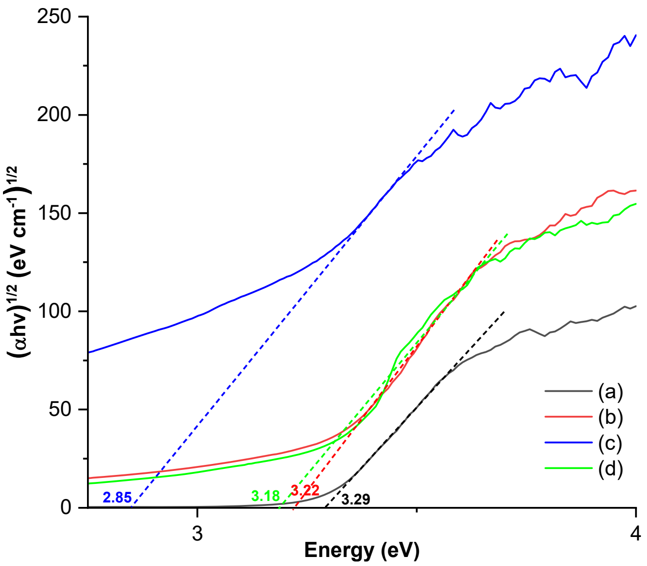

Fig 2. Tauc plot of (a) TiO_2, (b) TiO_2/Cr(100)-Cu(1), (c) TiO_2/Cr(200)-Cu(2), and (d) TiO_2/Cr(300)-Cu(3)

Table 1. The wavelengths of the absorption edge and band gap energy values of the TiO_2 photocatalysts

Photocatalyst	Wavelength (nm)	Band gap energy (eV)
TiO_2	377.8	3.29
TiO_2/Cr(100)-Cu(1)	385.2	3.22
TiO_2/Cr(200)-Cu(2)	435.7	2.85
TiO_2/Cr(300)-Cu(3)	390.1	3.18

Table 1 shows that the undoped TiO_2 exhibits an absorption wavelength in the UV range, whereas the doped photocatalysts display this phenomenon in the visible spectrum. Notably, doping Cr-Cu into the TiO_2 structure can effectively decrease the E_g value and narrow the gap, leading to a shift in light absorption from UV to the visible region. This alteration allows the doped TiO_2 to exhibit enhanced activity under visible light.

An intriguing pattern is apparent in Table 1, when the dopant amount increases, the reduction of E_g is more pronounced, with E_g decreasing and becoming less effective once the dopant amount is further increased. By introducing a greater amount of Cr-Cu, more of it can be doped, thus making it more effective in narrowing the gap. However, excessive amounts of the dopant may be prevented from entering the TiO_2 crystal lattice, resulting in only a small amount of it being doped and thus less narrowing of the gap.

XRD data

It is displayed in Fig. 3, the XRD patterns of the undoped and the doped TiO_2 photocatalysts. The XRD patterns of the doped TiO_2 are similar to the pattern of the undoped one, without being accompanied by any new peaks. The XRD patterns match with the XRD pattern of the anatase-typed TiO_2 standard. This data confirms that TiO_2 used in this research is anatase type having E_g 3.2 eV, which agrees with the E_g from the measurement (Table 1). Furthermore, it is noted in the XRD patterns of the doped TiO_2, that the intensities decline as the amount of the dopants is enlarged. Decreasing intensities are assigned to the lower crystallinity caused by partial TiO_2 structural destruction. The higher dopant amount is found to cause larger damage to TiO_2 crystallinity. This finding suggests that Cr-Cu has been successfully doped in the TiO_2 lattice crystal.

Photocatalytic Activity

Effect of the Cr-Cu doping

The activity of TiO_2 doped with Cr-Cu under visible irradiation is examined for degradation of LAS in real laundry wastewater. The results of the degradation are illustrated in Fig. 4. It shows that the LAS photodegradation over TiO_2 under visible light is observed to be less effective. The energy of the visible

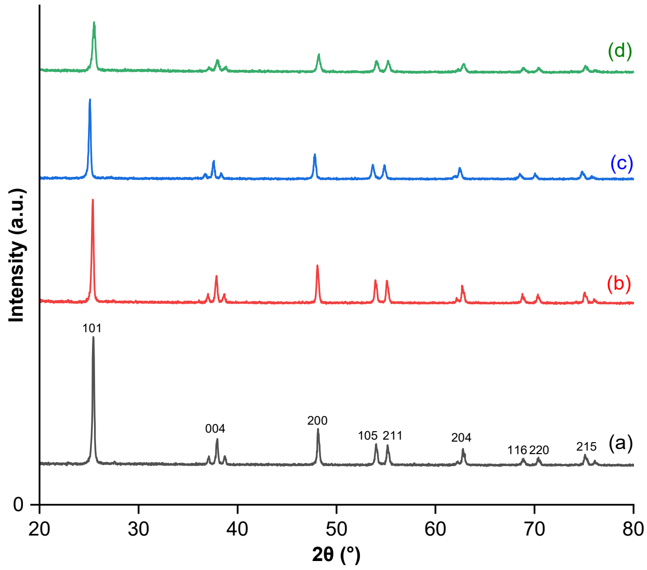

Fig 3. XRD patterns of (a) TiO_2, (b) TiO_2/Cr(100)-Cu(1), (c) TiO_2/Cr(200)-Cu(2), and (d) TiO_2/Cr(300)-Cu(3)

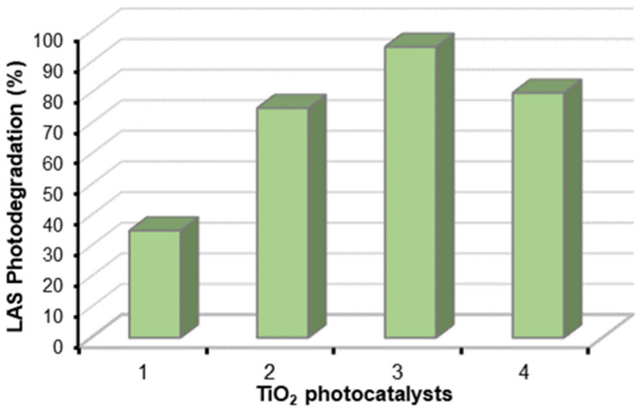

Fig 4. Effect of the dual doping on the photocatalyst activity under visible light, with (1) TiO_2, (2) TiO_2/Cr(100)-Cu(1), (3) TiO_2/Cr(200)-Cu(2), and (4) TiO_2/Cr(300)-Cu(3) (photocatalyst mass = 30 mg, reaction time = 60 min, solution pH = 7)

light (that is lower than 3.1 eV) is not adequate to excite the electrons and generate the OH from TiO_2, which has an E_g of 3.2 eV. Doping Cr-Cu can considerably enhance the photoactivity of TiO_2 under visible irradiation in the degradation of LAS in laundry wastewater. With the lower E_g values equal to the visible energy, TiO_2 doped with Cr-Cu can strongly absorb the visible light. As a result, a lot of OH radicals can be provided, which raises the effectiveness of LAS photodegradation. Moreover, increasing the dopant amount appears to give rise to LAS photodegradation, but a further increase in the dopant amount produces less effective photodegradation. This trend is in line with the E_g values. Increasing dopant amounts result in the lower E_g, where more visible light can be absorbed with the lower E_g, producing more OH radicals. The greater number of OH radicals promote higher effectiveness of the LAS degradation. The generation of OH radicals from TiO_2 under light irradiation and photodegradation are shown in Eq. (2-4).

$$TiO_2/Cr-Cu + \text{visible light} \rightarrow TiO_2/Cr-Cu\left(h^+ + e^-\right) \quad (2)$$

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+ \quad (3)$$

$$h^+ + R-C_6H_4-SO_3H \rightarrow CO_2 + H_2O + H_2SO_4 \quad (4)$$

However, further increase of the dopant amount leads to a detrimental LAS degradation. Excessive dopants are prevented from being inserted into the TiO_2 lattice, leading them to be dispersed at the outer side of the TiO_2 structure. In addition to reducing the visible light absorption and giving less OH radicals, this situation also inhibits the doped TiO_2 from contact with the LAS molecules.

Effect of the reaction time

The LAS degradation data from the process at various times is displayed in Fig. 5. The enhancement of degradation is observed when the reaction time is extended up to 60 min. The longer the irradiation time, the more effective contact between light and the photocatalyst can be achieved, which further enriches the formation of OH radicals. With a longer irradiation time than 60 min, the degradation effectiveness is seen independent of the irradiation time, since the surface of the photocatalyst has been saturated to provide OH radicals.

Effect of the photocatalyst mass

Fig. 5 also illustrates the effect of the photocatalyst mass on the LAS degradation. It can be revealed that enhancement of the LAS degradation can be obtained, as the photocatalyst mass is enlarged. Unfortunately, the opposite degradation data results when the photocatalyst mass is further increased over 30 mg. With the larger photocatalyst mass, more OH radicals can be generated, which produces more effective degradation. Advances in the increasing photocatalyst mass can generate higher turbid media, that filters the light penetration to contact with the photocatalyst and the media. Consequently, smaller OH radicals are available, further dismissing the LAS degradation.

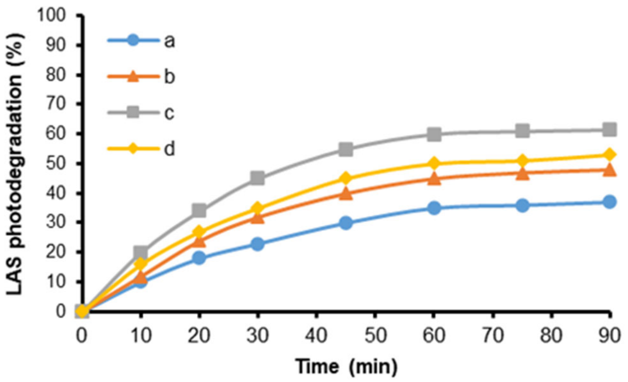

Fig 5. Effect of the reaction time on the LAS photodegradation over TiO_2-Cr(200)-Cu(2) with various masses, as (a) 10, (b) 20, (c) 30, and (d) 50 mg

Effect of the media pH

The LAS degradation result for the condition with pH alteration is presented in Fig. 6. As the media pH increases to 7, the LAS degradation is observed to rise and reach the maximum level. Further escalating pH until 10 leads to less effective LAS degradation. At low pH, both the surface of TiO_2 and the LAS structure are protonated to form positive charges, that repulse LAS to interact with TiO_2. This condition is not conducive to degradation. Increasing the pH to 7, less protonation or no protonation can occur, allowing TiO_2 to generate many OH radicals and adsorb LAS effectively. Such conducive conditions promote the highest degradation. In the media with a pH higher than 7, negative charges are formed in the TiO_2 surface and in the LAS structure, making the LAS degradation effective [31].

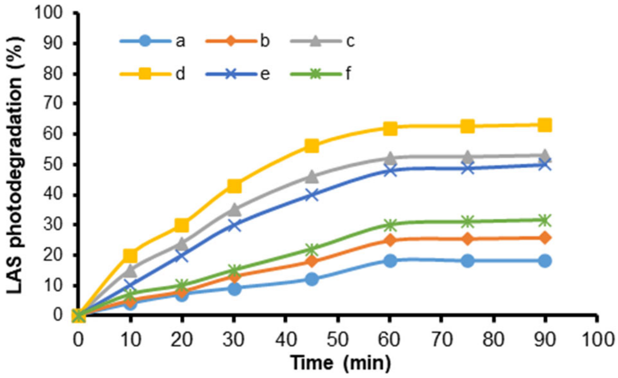

Fig 6. Effect of pH on the LAS photodegradation over TiO_2-Cr(200)-Cu(2) at pH (a) 1, (b) 3, (c) 5, (d) 7, (e) 9, and (f) 12 (photocatalyst mass = 30 mg)

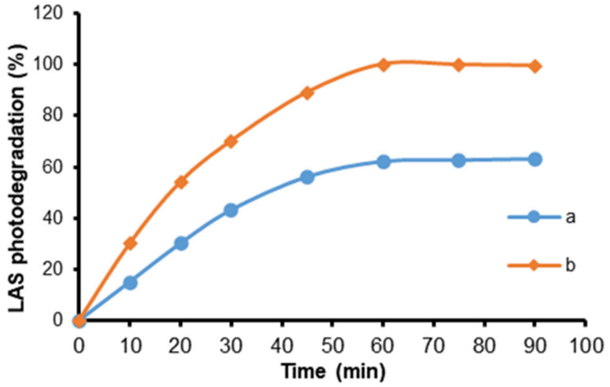

Fig 7. The LAS photodegradation results through (a) first and (b) second running of the photodegradation processes (TiO_2/Cr(200)-Cu(2) photocatalyst mass = 30 mg, solution pH = 7)

Repetition degradation

Under the optimum condition, the photodegradation rate of LAS with TiO_2-Cr(200)-Cu(2) was only around 60%, indicating that the doped photocatalyst had limited ability to degrade the LAS. To achieve a higher degradation rate, the laundry wastewater containing LAS was subjected to a second round of photodegradation under the same conditions using fresh TiO_2-Cr(200)-Cu(2). The results, depicted in Fig. 7, showed complete degradation of the LAS. The use of fresh doped photocatalysts resulted in a greater number of OH radicals, thus leading to more effective photodegradation of the LAS.

■ CONCLUSION

It can be concluded that the simultaneous doping of TiO_2 with Cr and Cu ions from electroplating wastewater has been successfully performed to decline the E_g values entering the visible region. The most effective E_g decreasing is shown by the medium amount of the dual dopant Cr and Cu (200:2) in TiO_2. In accordance with the decreasing E_g, the activity of the TiO_2 doped with dual dopants of Cr and Cu elements under visible light irradiation is enhanced significantly and the highest enhancement belongs to the TiO_2/Cr(200)-Cu(2) photocatalyst. The best condition for the degradation of the 125 mg/L LAS in 25 mL of the laundry wastewater over the photocatalyst of TiO_2/Cr(200)-Cu(2) under visible light is reached by using 30 mg of the photocatalyst mass, at pH 7, and in 60 min of the irradiation time reaching 60% of the degradation. Further, the LAS can be successfully degraded up to 100% by twice photodegradation runs.

■ ACKNOWLEDGMENTS

Authors greatly thank the Faculty of Mathematics and Natural Sciences Universitas Gadjah Mada for the financial support through the Project *"Dana Masyarakat"* Fund, with Contract Number: 116/J01.1.28/PL.06.02/2022, 2022.

■ CONFLICT OF INTEREST

The authors have no conflict of interest to declare.

■ AUTHOR CONTRIBUTIONS

All authors contributed to the study's conception and design. Sulistyaning Budi, Dea Aurellia, and Rizky Aprillia Widianti conducted the experiment. Endang Tri Wahyuni, Novianti Dwi Lestari, Nur Farhana Jaafar, and Suherman wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

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