

Synthesis of Iron-Doped Zirconium Titanate as a Potential Visible-Light Responsive Photocatalyst

Rian Kurniawan, Sri Sudiono, Wega Trisunaryanti, and Akhmad Syoufian*

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia

* Corresponding author:

email: akhmadsyoufian@ugm.ac.id

Received: September 7, 2018

Accepted: December 13, 2018

DOI: 10.22146/ijc.38616

Abstract: Synthesis and characterization of iron-doped zirconium titanate ($ZrTiO_4$) as a potential visible-light-responsive photocatalyst had been conducted. Various iron dopant concentrations and calcination temperature were investigated toward the properties of Fe-doped $ZrTiO_4$. The photocatalyst material was synthesized by sol-gel and impregnation method. Titanium tetraisopropoxide (TTIP) was used as a precursor, embedded on zirconia fine powder. A certain amount of iron (1, 3, 5, 7 and 9 wt.%) was introduced into the photocatalyst system from iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$). Photocatalyst with various iron concentrations was calcined at 500 °C. $ZrTiO_4$ with 5% iron was calcined at 700 and 900 °C. Characterization was performed by using XRD, FT-IR, SR-UV, and SEM-EDX. The presence of iron on the surface of $ZrTiO_4$ was proved by EDX analysis. Fe-doped $ZrTiO_4$ with the lowest bandgap (2.83 eV) is 7% of iron content after calcination at 500 °C.

Keywords: Fe-doped $ZrTiO_4$; photocatalyst; iron; dopant; bandgap

■ INTRODUCTION

Zirconium dioxide or zirconia (ZrO_2) is one of the potential materials for photocatalysis due to its unique properties. It exhibits a high refractive index, optical transparency, high corrosive resistance, high mechanical properties, high thermal expansion, low thermal conductivity, high chemical and photothermal stability [1]. Wide bandgap of ZrO_2 (~5 eV) gives very strong photo-generated redox ability under ultra-violet (UV) irradiation [2]. Apparently, due to its wide bandgap, ZrO_2 is not effective under solar irradiation.

Titanium dioxide (TiO_2) is considered as the most potential photocatalyst material due to its relatively strong oxidizing power under UV irradiation, high chemical stability, relatively cheap, and environmentally friendly [3]. Titanium dioxide or titania exists in four polymorphs which are anatase, rutile, brookite, and $TiO_2(B)$. Rutile is the most stable form at ambient pressure and temperature in macroscopic sizes while anatase is more stable in nanoscopic sizes [4]. The bandgap is 3.0 eV for rutile and 3.2 eV for anatase [5]. By combining TiO_2 with ZrO_2 , it will produce a composite

material called zirconium titanate ($ZrTiO_4$) which expected to have a smaller bandgap than that of ZrO_2 .

Zirconium titanate is a semiconductor material with high dielectric properties and very corrosive resistant. It exists in the orthorhombic structure at 400 °C calcination. Its bandgap was reported to be around 3.4 eV, which is relatively more photo-active than ZrO_2 [6]. Other study had shown the potential application of $ZrTiO_4$ as a photocatalyst material, but it does not perform as efficiently as TiO_2 because of its relatively wide bandgap [7]. Thi et al. investigated the calcination temperature of the $ZrTiO_4$ system towards the bandgap. Higher calcined $ZrTiO_4$ has a wide bandgap [8].

Iron(III) metal ion (Fe^{3+}) was proved to be good dopant for increasing photocatalytic performance of TiO_2 . Due to its ionic radii similar to Ti^{4+} , Fe^{3+} is able to incorporate into the TiO_2 crystal structure and acts as a recombination center. The d^5 valence electronic configuration of Fe^{3+} increases stability [3]. Incorporation of Fe^{3+} into ZrO_2 crystal structure also decreases the bandgap and increases the photocatalytic activity, although its efficiency is still low if compared to TiO_2

system [9]. By introducing Fe^{3+} ion into ZrTiO_4 crystal structure, it will shift the bandgap and increase absorption efficiency towards visible light.

Several works have reported that modifications to shift the absorption of ZrTiO_4 towards visible region can be done by varying Ti:Zr weight ratio [10], creating hollow sphere shape [11] and doping with Bi_2O_3 [12]. However, all results still had relatively high bandgap (above 3.0 eV). Castillo et al. have successfully synthesized iron doped TiO_2 nanoparticles by using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as an iron source [13]. In this research, Fe-doped ZrTiO_4 will be synthesized by sol-gel method. Various iron concentrations as a dopant were introduced into the ZrTiO_4 system and calcined at different temperatures to observe the optical properties of the resulted Fe-doped ZrTiO_4 . A certain amount of iron in ZrTiO_4 system with optimum calcination temperature is expected to result in Fe-doped ZrTiO_4 with high responsive towards sunlight.

■ EXPERIMENTAL SECTION

Materials

Titanium(IV) tetraisopropoxide (TTIP) (97%, Sigma-Aldrich) and zirconia (ZrO_2) fine powder (Jiaozuo Huasu) were used as precursors for synthesizing the photocatalyst material. Iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Merck) was used as the dopant source. Solvents were absolute ethanol (PA, Merck) and demineralized water (Jaya Sentosa).

Instrumentation

Crystal structures of the samples were analyzed with X-ray powder diffractometer (XRD) PANalytical X'Pert PRO MRD. Surface structure was observed with scanning electron microscopy equipped with energy dispersive X-ray spectrometer (SEM-EDX) JSM-6510LA. Fourier-Transform infrared spectrometer (FT-IR) analysis was conducted using Thermo Nicolet iS10. Ultraviolet and visible (UV-Vis) absorption of the samples were measured by specular reflectance UV-Vis spectrophotometer (SRUV) UV1700 Pharmaspec.

Procedure

First, 2.5 mL (8.2 mmol) of TTIP was dissolved in

25 mL of absolute ethanol, while 1 gram (8.1 mmol) of ZrO_2 powder was dissolved in 25 mL of demineralized water. A certain amount of iron salts (1, 3, 5, 7 and 9 wt.%) was also dissolved into ZrO_2 suspension. Then, the suspension was dropped into TTIP solution under mild stirring and followed by vigorous stirring for 30 min [14]. The suspended solid was separated by centrifugation at a rate of 1500 rpm for 1 h. Obtained solid was aged at 27 °C for 48 h and then heated at 50 °C for 24 h. The composite material was calcined at 500, 700 and 900 °C under atmospheric condition for 4 h.

■ RESULTS AND DISCUSSION

Fe-doped ZrTiO_4 had been successfully synthesized. Fig. 1 shows the diffraction pattern of various iron contents in ZrTiO_4 together with reference materials ZrO_2 and TiO_2 . All of the samples were calcined at 500 °C. ZrO_2 reference corresponds to a monoclinic structure (JCPDS: 37-1484) as characteristic diffraction peaks appeared at 24.1° (011), 28.2° (-111), 31.5° (111) and 34.1° (002). No metastable tetragonal pattern was observed. Only anatase structure (JCPDS: 21-1272) appeared in TiO_2 reference at 25.4° (101). Fe-doped ZrTiO_4 samples had strong monoclinic ZrO_2 pattern, while anatase pattern was hardly observable and no iron pattern. It happened because of the amount of iron and TiO_2 in Fe-doped ZrTiO_4 are very small compared to ZrO_2 . Fe-doped ZrTiO_4 diffractions reveal that the relative intensity of anatase peak around 25° (101) decreased from 18 to 9%, as iron content increased. It may be caused by iron dopant promoting phase transformation of anatase into rutile [15]. Another report suggests that Zr^{4+} inhibits the anatase-rutile transformation [16]. ZrO_2 probably hinders the formation of rutile; thus there was no rutile peak observed.

Fig. 2 shows the diffraction pattern of 5% Fe-doped ZrTiO_4 calcined at different temperatures together with reference materials consisting TiO_2 at different calcination temperatures and ZrO_2 after 500 °C calcination. Same as the previous description, the diffraction pattern of ZrO_2 and TiO_2 after 500 °C calcination only showed monoclinic and anatase, respectively. TiO_2 after 700 °C

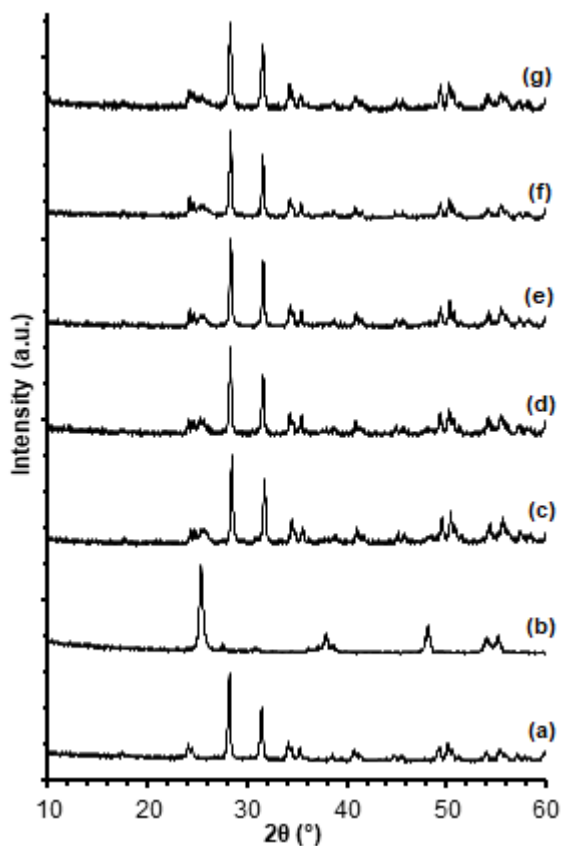


Fig 1. Diffraction pattern of (a) ZrO_2 , (b) TiO_2 , $ZrTiO_4$ with (c) 1%, (d) 3%, (e) 5%, (f) 7% and (g) 9% of Fe content after calcination at 500 °C

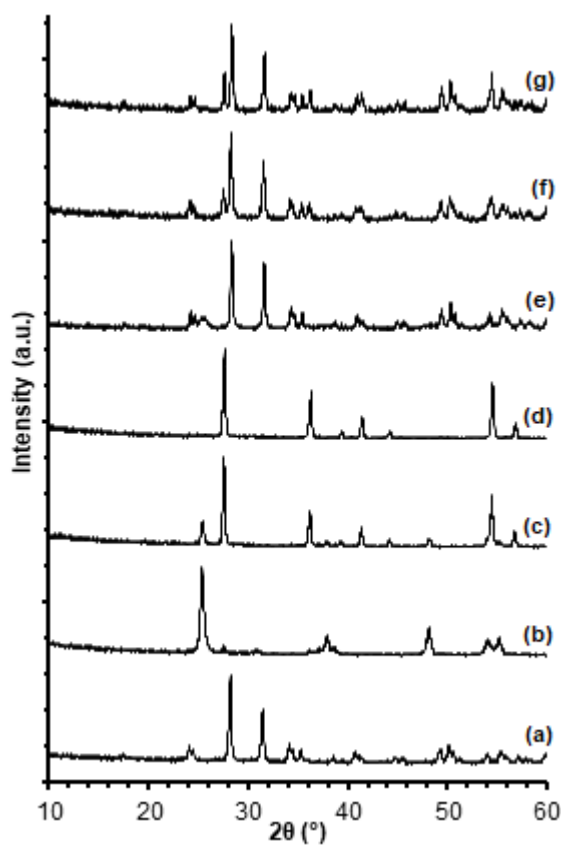


Fig 2. Diffraction pattern of (a) ZrO_2 500 °C, TiO_2 (b) 500 °C, (c) 700 °C, (d) 900 °C, 5% Fe-doped $ZrTiO_4$ (e) 500 °C, (f) 700 °C and (g) 900 °C

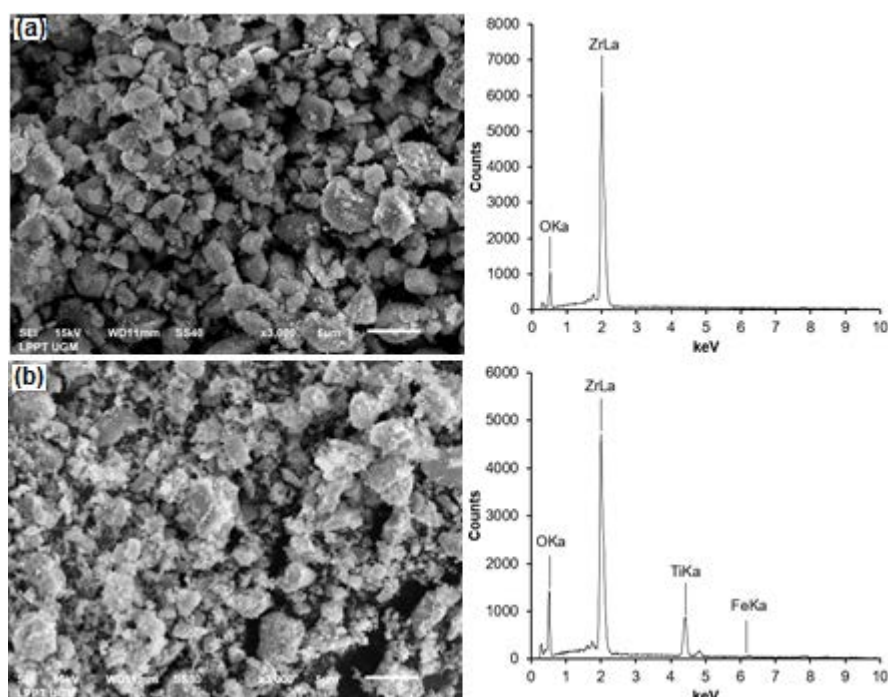


Fig 3. SEM images and EDX spectra of (a) ZrO_2 and (b) 5% Fe-doped $ZrTiO_4$ after calcination at 700 °C

calcination showed characteristic rutile pattern (JCPDS: 21-1276) at 27.6° (110), 36.2° (101), 41.4° (111) and 54.5° (211), while the intensity of anatase pattern at 25.5° (101) and 48.2° (200) decreased. Only rutile pattern appeared in diffraction of TiO_2 after 900°C . The diffraction pattern of Fe-doped ZrTiO_4 samples revealed that rutile structure starts to appear after 700°C calcination corresponding to rising peak at 27.5° (110) and 36.1° (101). Anatase pattern was completely disappeared as the intensity of rutile pattern arose at Fe-doped ZrTiO_4 after 900°C calcination.

Fig. 3 presents SEM images and corresponding EDX analysis of ZrO_2 and 5% Fe-doped ZrTiO_4 after calcination at 700°C . The surface of Fe-doped ZrTiO_4 was more rugged than ZrO_2 , due to iron and TiO_2 deposition. It was confirmed with EDX analysis in Fig. 3, summarized in Table 1. The observed percentage of iron was very small, thus explains its absence in the X-ray diffraction pattern. The difference between measured and theoretical iron percentage is due to chemical equilibrium during the sol-gel reaction. Sol-gel reaction was performed without controlling the pH. Not all iron(II) precipitated into the formed sol. The amount of iron added while preparation was purposely excess due to anticipating the chemical equilibrium by reaction condition. Metal should be introduced in a small amount to obtain an optimal doping effect. The ratio of Zr to O became lower than in ZrO_2 due to the presence of TiO_2 on the surface of iron-doped ZrTiO_4 . Fe-doped ZrTiO_4 particles looked similar to ZrO_2 particles with an estimated diameter around 2–5 μm .

Fig. 4 presents FT-IR spectra of various iron dopant concentrations in ZrTiO_4 with ZrO_2 and TiO_2 as references. All the samples were calcined at 500°C . Vibration band around 3400 cm^{-1} appearing in all samples are identified as O–H vibration. ZrO_2 vibrational band at 740 cm^{-1} is attributed to Zr–O₂–Zr asymmetric mode of monoclinic [17]. The vibrational band around 490 cm^{-1} belongs to Zr–O vibration [1]. The broad vibrational band around 500 cm^{-1} of reference TiO_2 is designated to stretching vibration of Ti–O mode [18]. There is a vibrational band that appeared and increased around 1120 cm^{-1} as iron concentration arose on Fe-doped ZrTiO_4 spectra. It may belong to either Fe–O–Zr or Fe–O–Ti, or also possibly both.

Table 1. EDX analysis of ZrO_2 and 5% Fe-doped ZrTiO_4 after calcination at 700°C

Samples	% Mass				
	Zr	O	Ti	Fe	Total
ZrO_2	73.49	26.51	-	-	100
5% Fe-doped ZrTiO_4	52.36	34.08	12.72	0.85	100

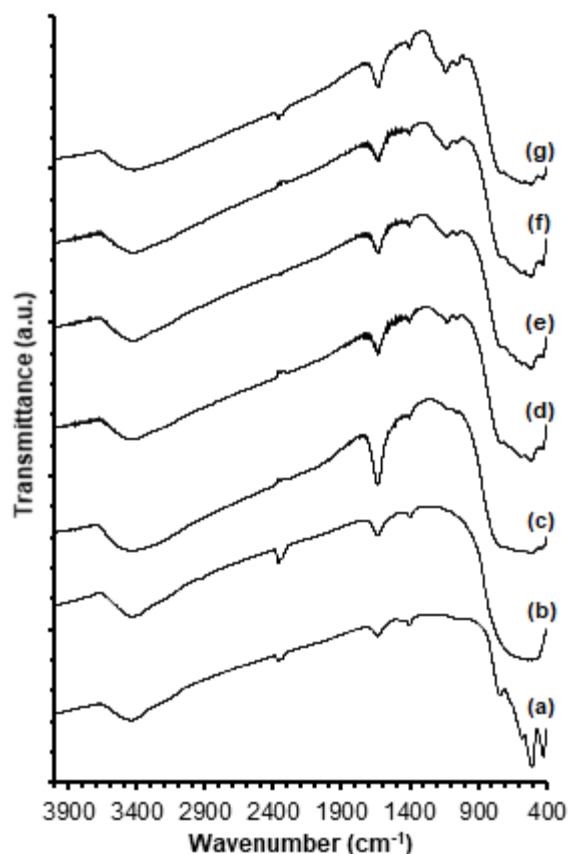


Fig 4. FT-IR spectra of (a) ZrO_2 , (b) TiO_2 and ZrTiO_4 with (c) 1%, (d) 3%, (e) 5%, (f) 7% and (g) 9% of Fe content after calcination at 500°C

Fig. 5 presents FT-IR spectra of iron-doped zirconium titanate after calcination at different temperatures with TiO_2 and ZrO_2 as references. Higher calcination temperature on TiO_2 reduces the intensity of O–H vibration at 3400 cm^{-1} and sharpens Ti–O stretching mode around 500 cm^{-1} . The iron dopant vibration band on the samples around 1120 cm^{-1} decreased as calcination temperature increased. This possibly happened because of the iron dopant that sinters at a higher temperature, thus the Fe–O vibration weakens.

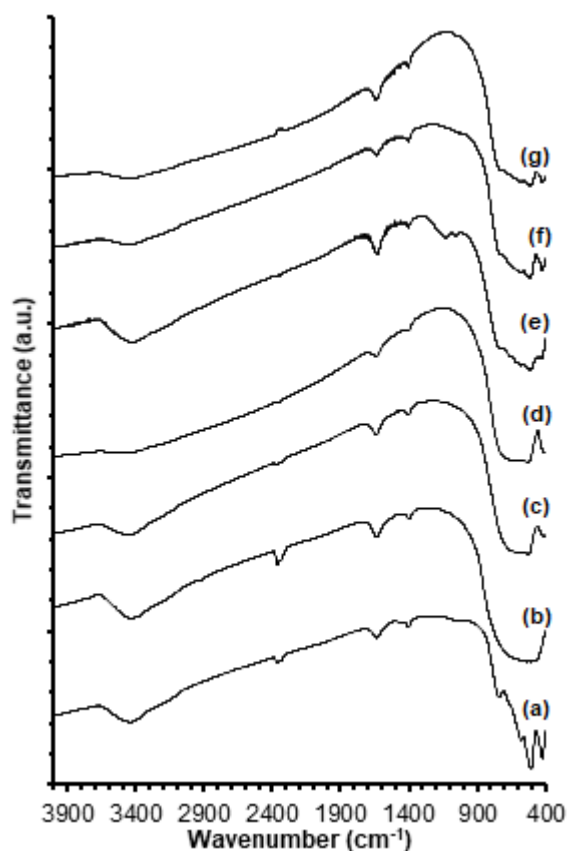


Fig 5. FT-IR spectra of (a) ZrO₂ 500 °C, TiO₂ (b) 500 °C, (c) 700 °C, (d) 900 °C, 5% Fe-doped ZrTiO₄ (e) 500 °C, (f) 700 °C and (g) 900 °C

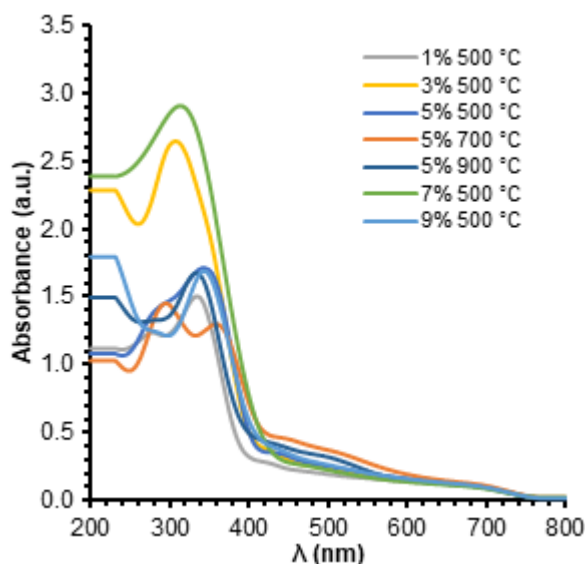


Fig 6. UV-Vis absorption spectra of various Fe-doped ZrTiO₄

Table 2. Bandgap data of Fe-doped ZrTiO₄ with ZrO₂ and TiO₂

Sample	E _g (eV)
ZrO ₂ 500 °C	3.23
TiO ₂ 500 °C	3.02
Fe-doped ZrTiO ₄ 1% 500 °C	2.96
Fe-doped ZrTiO ₄ 3% 500 °C	2.88
Fe-doped ZrTiO ₄ 5% 500 °C	2.85
Fe-doped ZrTiO ₄ 5% 700 °C	2.93
Fe-doped ZrTiO ₄ 5% 900 °C	2.97
Fe-doped ZrTiO ₄ 7% 500 °C	2.83
Fe-doped ZrTiO ₄ 9% 500 °C	2.88

The bandgap of photocatalyst material can be obtained by analyzing spectral data of UV-Vis absorption. Bandgap relates to the absorption edge of the photocatalyst. Spectral data of photocatalyst material generally consist of single or more absorption peaks. Absorption edge can be determined by finding a turning point which exhibits minimum absorbance at the edge of the absorption peak. Fig. 6 shows UV-Vis absorption spectra of iron-doped ZrTiO₄, whereas Table 2 summarizes the bandgap value from UV-Vis absorption data analysis. All Fe-doped ZrTiO₄ samples exhibited lower bandgap than ZrO₂ and TiO₂. The iron dopant is proved to decrease the indirect bandgap of ZrTiO₄ as iron content increases from 1 to 7%. The new energy level is formed between the valence and conduction band of ZrTiO₄. As the iron concentration increased, the density of new energy levels formed also increased, thus lowering the bandgap. The bandgap increased from 7 to 9%, due to the heterojunction effect that cancels the doping effect. The bandgap of ZrTiO₄ with 5% of iron content increased as the calcination temperature was increased. This phenomenon probably happened because iron dopant is sintered. There are two peaks appearing on the samples that had been calcined at 700 and 900 °C. Those two peaks are attributed to the monoclinic and rutile phase.

Based on the optical properties, all Fe-doped ZrTiO₄ is expected to be responsive towards the visible-light region. Due to its relatively small bandgap,

Fe-doped ZrTiO₄ should be a potential candidate as photocatalyst material under sunlight irradiation.

■ CONCLUSION

Iron-doped zirconium titanate had been successfully synthesized by sol-gel method. XRD characterization signifies that iron concentration and calcination temperature alter the phase composition of the iron-doped ZrTiO₄ composite. The presence of TiO₂ and iron on ZrTiO₄ surface were proved by SEM-EDX. Doping of iron into ZrTiO₄ shifts the bandgap to be lower than ZrO₂ and TiO₂, which is believed to be more responsive towards visible region. On the contrary, higher calcination temperature induces the iron-doped ZrTiO₄ to be more responsive towards the UV region. ZrTiO₄ with 7% iron after calcination at 500 °C happens to have the lowest bandgap ($E_g = 2.83$ eV). Thus, making it possible to apply the composite as a catalyst under visible-light irradiation.

■ ACKNOWLEDGMENTS

We would like to express our gratitudes to The Ministry of Research, Technology and Higher Education of the Republic of Indonesia for their support on this works through PDUPT 2018 Grant (73/UN1/DITLIT/DIT-LIT/LT/2018).

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