Synthesis and characterization of Al-Fe-Cu tri-doped TiO$_2$ by in-situ hydrothermal for degradation of methylene blue dyes

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Abstract. Pure TiO$_2$ and a series of Al-Fe-Cu tri-doped TiO$_2$ were synthesized by using in-situ hydrothermal method. The synthesized materials were characterized using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM). The photocatalytic activity of the samples was evaluated for degradation of methylene blue (5mgL$^{-1}$) in aqueous solution under uv-visible light ($\lambda<420$ nm). The XRD pattern showed that all samples exhibited anatase phase after calcined at temperature 500°C with crystallite size in the range of 10.00-13.23 nm. The FTIR spectra showed three important vibrational modes for $\nu$OH, $\delta$OH and $\nu$TiO that were assigned at range 3411.75-3399.27 cm$^{-1}$, 1626.91-1630.53 cm$^{-1}$ and 503.30-530.93 cm$^{-1}$, respectively. The degradation rate of Al(1mmol)-Fe-Cu tri-doped TiO$_2$ showed the highest photocatalytic degradation with 93% compared to pure TiO$_2$, Al(2 mmol)-Fe-Cu tri-doped TiO$_2$ and Al(3mmol)-Fe-Cu tri-doped TiO$_2$ were calculated as 76%, 85% and 80%, respectively. Hence, it can be seen that, the amount of Al ion-doping have influence on the photocatalytic degradation.

1. Introduction

Nowadays, waste water is the major pollution to the environmental issues. On a daily industrial and basis activities, huge amount of organic and inorganic dyes uncontrolled released in our rivers and seas. Effect from the continual exposure to this dyes can threatened humankind health such as irritations, toxic effects, and limitation to the safe drinking water [1]. Thus, science was interested in searching any low cost alternatives and environmentally friendly methods for filtering up waste water contamination. Recently, tremendous efforts have been devoted to minimize percentage issues of waste water contamination by using a filtration process from semiconductor materials. Among the studies of semiconductor materials, TiO$_2$ have received much attention due to their good performance such as high efficient photo catalytic activity, high refractive index, high chemical stability, nontoxicity and low cost [2]. However, TiO$_2$ suffer from some limitations, due to its large band gap, which around 3.0 eV and 3.2 eV for anatase and rutile respectively, occupy only 3-5% of total solar spectrum [3]. On the other hand, performance of photocatalytic activity might be decreased because of the fast recombination of photogenerated electron-hole pairs [4-5].

Therefore many studies have been reported to enhance the photocatalytic activity performance such as widen the absorption scope of TiO$_2$ to visible region and reduce the recombination of electron-holes. Previous study has reported that addition of dopant into TiO$_2$ lattice is commonly be used to increase the photocatalytic activities under visible light [6]. Selection of doping TiO$_2$ from metal such as Ce, La, Bi,
and Mg and non-metal ions such as N, S and C have been reported to prolong the absorption edge and could enhance the photocatalytic activities under visible light [7]. Xing et al. (2010) reported that, tri-dopant is better than co-dopant and single-dopant because of metal ions from tridopant can trap the photogenerated electrons and holes, which increasing photocatalytic activity [8]. However tri-dopant TiO$_2$ nanostructures for both nanoparticles and nanotubes are still in limited study and rarely reported. Hence, our study is to examine the effect of metals ion used as tri-dopant towards photocatalytic activity. In this study, Al$_{1(1mmol)}$-Fe-Cu tri-doped TiO$_2$, Al$_{2(2mmol)}$-Fe-Cu tri-doped TiO$_2$ and Al$_{3(3mmol)}$-Fe-Cu tridoped TiO$_2$ were synthesized by in-situ hydrothermal method. In-situ hydrothermal process was chosen due to easy preparation method and high capability to form large surface area of nanostructure materials. In this case study, aluminium (Al) ion, iron (Fe) ion or copper (Cu) ion has been selected as dopants since they have highly abundance on the earth’s crust, low cost, can reducing the electron and holes recombination rates, most stable in the presence of sulfuric acid and owned smaller ionic radii compared to Ti$^{4+}$ [9-12].

In-situ hydrothermal method involved of two stages including stirring and sonication to increase concentration of TiO$_2$ with NaOH solution as well as ended with washing process with HCl-dionized water to promote ionic exchange from Na$^+$ in TiO$_2$ and H$^+$ in HCl and deionized water. The effects of various amount of aluminium (III) nitrate nanohydrate were used to optimize the tri-dopant towards degradation study.

2. Experimental
2.1 Preparation
In this study all compounds, pure TiO$_2$, Al$_{1(1mmol)}$-Fe-Cu tri-doped TiO$_2$, Al$_{2(2mmol)}$-Fe-Cu tri-doped TiO$_2$ and Al$_{3(3mmol)}$-Fe-Cu tri-doped TiO$_2$ were synthezised by in-situ hydrothermal method. 2 g of titanium dioxide powder, aluminium (II) nitrate nanohydrate (1 mmol, 2 mmol and 3 mmol), 1 mmol of iron (III) nitrate nanohydrate and 1 mmol of copper (II) nitrate trihydrate were dispersed in an aqueous solution of 10M NaOH (100 mL) and placed in a stainless-steel with Teflon lining reactor. Then, the reactor was transferred into an autoclave. The autoclave was heated at 150°C for 24 hours. After the treatment, the resultant precipitate was separated by centrifugation and washed with diluted HCl solution until pH 7. The sample was dried in an oven at 80°C for 24 hours. After drying, the obtaining powder was calcined at 500°C. Pure TiO$_2$ also was synthesized by using similar procedure, but without the presence of tri-dopant, aluminium (III) nitrate nanohydrate, iron (III) nitrate nanohydrate and copper (II) nitrate trihydrate.

2.2 Characterization
The X-Ray Diffraction (XRD) pattern was collected by using Rigaku Miniflex with Cu-K$_\alpha$ (0.1541 nm) at scan rate from 10°- 80° (2θ). Crystallite size was calculated by using Scherrer’s Equation as stated below [13]

$$Scherrer’s\ equation\ (D) = \frac{k\lambda}{\beta \cos \theta}$$

Where (D =crystallite size in nm);
K= 0.9 constant
$\lambda$= 0.1541 nm (wavelength of the X-ray radiation)
$\beta$= FWHM (full width at half maximum)
$\theta$= the diffraction angle

Infrared analysis was used to determine and identify functional groups present in pure TiO$_2$ and Al-FeCu tri-doped TiO$_2$ series. The model of FTIR used is Perkin Elmer Spectrum 100 with recorded in range of 4000-400 cm$^{-1}$ utilizing potassium bromide (KBr) pellet. SEM micrographs were captured using JSM 6360 Joey Scanning Electron Microscopy with accelerated voltage 20kV and magnification from 10000X.
2.3 Photocatalytic degradation test
The photocatalytic degradation test was examined by adding 5mg of samples into 100ml of 5 ppm methylene blue dye solution [13-14]. The solution was directed to UV lamp for 1 hour and continues stirring. At every 10 minutes of interval time, 5ml of the solution was taken out by using syringe and filtered through 0.45 um milipore syringe filter to separate the powder from the supernatant. The absorption was recorded via UV-vis spectrophotometer (Spectrophotometer Shimadzu UV-1800).

3. Results and discussion
Figure 1 shows the XRD pattern of the prepared samples. It can be concluded that the diffraction peaks of all studied samples were represented to anatase TiO\textsubscript{2} phase as at 2θ = 25.26°, 37.78°, 48.00°, 53.93°, 55.03°, 62.78°, 70.19° and 74.98°. Anatase peak was formed by treating with 10M NaOH aqueous solution at 150°C for 24 hours and calcined at 500°C. Washing part has been introduced to eliminate Na\textsuperscript{+} from Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} (titanate) (1). Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} was treated by using 0.1M of HCl and distilled water to form H\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7} (3). At this stage, H\textsuperscript{+} from HCl promoted ion exchange of Na\textsuperscript{+}. Generally, formation of TiO\textsubscript{2} anatase (5) reaction was occurred as stated below;

\[
\begin{align*}
3\text{TiO}_2 (\text{commercial}) + 2\text{NaOH} & \rightarrow \text{Na}_2\text{Ti}_3\text{O}_7 + \text{H}_2\text{O} & (2) \\
\text{Na}_2\text{Ti}_3\text{O}_7 + 2\text{HCl} & \rightarrow \text{H}_2\text{Ti}_3\text{O}_7 + 2\text{NaCl} & (3) \\
\text{H}_2\text{Ti}_3\text{O}_7 & \rightarrow \text{TiO}_2 + \text{H}_2\text{O} & (4) \\
\text{H}_2\text{Ti}_3\text{O}_7 & \text{calcinated at 500°C} \rightarrow \text{TiO}_2(\text{anatase}) & (5)
\end{align*}
\]

The XRD pattern also shows that there has no phase change in TiO\textsubscript{2} during addition of tri-dopant process and calcination at 500 °C. Furthermore, peak for Al\textsuperscript{3+}, Fe\textsuperscript{3+} and/or Cu\textsuperscript{2+} did not observed at XRD patterns. This is might be due to lower amount of aluminium (III) nitrate nanohydrate, iron (III) nitrate nanohydrate and copper (II) nitrate trihydrate used in the synthesis. In other hand, this is proving that, all the dopants successfully incorporated into the lattice site of TiO\textsubscript{2}, since ionic radii of Al\textsuperscript{3+}(0.39Å), Fe\textsuperscript{3+}(0.58Å) and Cu\textsuperscript{2+} (0.57Å) are smaller than ionic radii of Ti\textsuperscript{4+} (0.65Å) [15]. Table 1 showed that, the crystallite size of Al\textsubscript{1}(1mmol)-Fe-Cu tri-doped TiO\textsubscript{2}, Al\textsubscript{1}(2mmol)-Fe-Cu tri-doped TiO\textsubscript{2} and Al\textsubscript{1}(3mmol)-Fe-Cu tri-doped TiO\textsubscript{2}.

![XRD patterns](image)

**Figure 1.** XRD patterns of pure TiO\textsubscript{2}, Al\textsubscript{1}(1mmol)-Fe-Cu tri-doped TiO\textsubscript{2}, Al\textsubscript{1}(2mmol)-Fe-Cu tri-doped TiO\textsubscript{2} and Al\textsubscript{1}(3mmol)-Fe-Cu tri-doped TiO\textsubscript{2}.
doped TiO₂ were found to be 10.00 nm, 10.57 nm and 11.29 nm, respectively. The crystallite sizes of tri-dopant were much smaller compared to pure TiO₂. Therefore, the smaller crystallite size contributes to the large surface area and high volume of pores resulting to the rapid adsorption-oxidation reaction occur [15].

Table 1. The average crystallite size

| Sample                                      | Crystallite size (nm) |
|---------------------------------------------|-----------------------|
| Pure TiO₂                                   | 13.23                 |
| Al₁(mmol)⁻Fe⁻Cu tri-doped TiO₂              | 10.00                 |
| Al₂(mmol)⁻Fe⁻Cu tri-doped TiO₂              | 10.57                 |
| Al₃(mmol)⁻Fe⁻Cu tri-doped TiO₂              | 11.29                 |

FTIR spectra of pure TiO₂, Al₁(mmol)⁻Fe⁻Cu tri-doped TiO₂, Al₂(mmol)⁻Fe⁻Cu tri-doped TiO₂ and Al₃(mmol)⁻Fe⁻Cu tri-doped TiO₂, respectively as shown in Figure 2. The FTIR spectra showed that three important vibrational modes for νOH, δOH and νTiO were assigned at range 3411.75-3399.27 cm⁻¹, 1626.91-1630.53 cm⁻¹ and 503.30- 530.93 cm⁻¹, respectively. The νOH clearly observed in the spectra due to the physisorbed water molecule that present in the surface of TiO₂.

![Figure 2. FTIR spectra of pure TiO₂ and Al-Fe-Cu tri-doped TiO₂ series](image)

Based on the IR spectra, the peak Ti-O-Ti stretching of pure TiO₂ showed the lowest frequency which is 503.30 cm⁻¹. However, after the addition of dopants into TiO₂, the vibration of Ti-O-Ti stretching started to change to the higher frequency. This is might be due to the distribution of dopants in the molecules that shifted the Ti-O-Ti stretching into the high frequency.

SEM images of the pure TiO₂ and Al-Fe-Cu tri-doped TiO₂ series powder were represented in Figure 3. All of samples revealed that spherical structures aggregated and have several long fibres were found assembled together. This finding is in agreement with the results as reported by Razali et al., 2014 [15]. From visual inspection of SEM morphology, nanotubes were expected successfully obtained. In contrast, the synthesized pure TiO₂ has larger particle size than tri-dopant as reliable with the crystal size estimation from XRD analysis (Table 1). However, to confirm the obtaining nanotubes, TEM analysis should be done in future.
Figure 3. SEM images of (a) pure TiO$_2$, (b) Al$_{1\text{mmol}}$-Fe-Cu tri-doped TiO$_2$, (c) Al$_{2\text{mmol}}$-Fe-Cu tridoped TiO$_2$ and (d) Al$_{3\text{mmol}}$-Fe-Cu tri-doped TiO$_2$ viewed under 10000x magnification.

The degradation photocatalytic was study by using different interval time towards irradiation. 5ppm of methylene blue solution was used to evaluate the performance of all samples upon discoloration. The degradation rates for all samples were determined by using formula as stated below:

$$\text{degradation (\%) } = \frac{C_0 - C_1}{C_0} \times 100\%$$

Figure 4 shows the degradation rate of Al$_{1\text{mmol}}$-Fe-Cu tri-doped TiO$_2$ sample exhibited the highest photocatalytic degradation, with 93% compared to the pure TiO$_2$, Al$_{2\text{mmol}}$-Fe-Cu tri-doped TiO$_2$ and Al$_{3\text{mmol}}$-Fe-Cu tri-doped TiO$_2$ were calculated as 76%, 85% and 80%, respectively. As expected, Al$_{1\text{mmol}}$-Fe-Cu tri-doped TiO$_2$ showed the highest photocatalytic degradation due to smaller crystallite size (10.00 nm) that fasten the degradation process. The principle of photocatalytic study is, when a distortion occurs because of the addition of any dopants into the lattice site of TiO$_2$, the TiO$_2$ crystallization maybe increased [16]. The surface area would be larger thus increasing the photocatalytic degradation [9]. Based on this fact, it can be seen that the presence of a small amount of Al$^{3+}$ dopant in TiO$_2$ can enhance the photocatalytic degradation of methylene blue. Thus, 1mmol of aluminium (III) nitrate nanohydrate that used in this study perhaps is the best amount to the optimum level.
The mechanism throughout this case study may be summarized as previous study by equation below (6-16) [9,12,15].

\[
\begin{align*}
\text{TiO}_2 + hv &\rightarrow h^+ + e^- \\
\text{Ti}^{4+} + e^- &\rightarrow \text{Ti}^{3+} \\
\text{O}_2 + h^+ &\rightarrow \text{O} \\
\text{Cu}^{2+} + \text{Ti}^{3+} &\rightarrow \text{Cu}^+ + \text{Ti}^{4+} \quad \text{electron trap} \\
\text{Fe}^{3+} + \text{O}^- &\rightarrow \text{Fe}^{2+} + \text{O}^2^- \quad \text{hole trap} \\
\text{Fe}^{3+} + \text{OH} &\rightarrow \text{Fe}^{2+} + \text{OH} \quad \text{hole release} \\
\text{Cu}^+ + \text{O}_2 &\rightarrow \text{Cu}^{2+} + \text{O}_2^- \quad \text{electron release} \\
\text{Al}^{3+} + \text{O}^- &\rightarrow \text{Al}^{2+} + \text{O}_2^- \quad \text{hole trap} \\
\text{Al}^{3+} + \text{Ti}^{3+} &\rightarrow \text{Al}^{2+} + \text{Ti}^{4+} \quad \text{electron trap} \\
\text{Al}^{3+} + \text{OH} &\rightarrow \text{Al}^{2+} + \text{OH} \quad \text{hole release} \\
\text{Al}^{3+} + \text{O}_2 &\rightarrow \text{Al}^{2+} + \text{O}_2^- \quad \text{electron release} \\
\text{Dye} + \text{O}_2^- + \text{OH} &\rightarrow \text{The degraded product}
\end{align*}
\]

This study also revealed that, these three metal ions used, Al\(^{3+}\), Fe\(^{3+}\) and Cu\(^{2+}\) were proven gave the excellent performance towards photocatalytic degradation of methylene blue by reducing the recombination. As comparison, pure TiO\(_2\) degraded only 78% of methylene blue after 10 minutes reaction due to the electrons and holes were recombined and affected the degradation process to the lowest rate [15]. However, Al\(^{3+}\) dopant may give the major contribution due to have smallest ionic radii. The insertion of Al\(^{3+}\) ion easily enter into lattice site of Ti\(^{4+}\) managed to create a trap site for electrons and holes thus, contributed to the highest photocatalytic activity.

4. Conclusion
Pure TiO\(_2\) and a series of Al-Fe-Cu tri-doped TiO\(_2\) were successfully synthesized by using in-situ hydrothermal method. All samples exhibited anatase phase after calcined at temperature 500°C with crystallite size in the range of 10.00-13.23 nm. The FTIR spectra showed three important vibrational modes for \(\nu\text{OH}, \delta\text{OH}\) and \(\nu\text{TiO}\) that were assigned at range 3411.75-3399.27 cm\(^{-1}\), 1626.91-1630.53 cm\(^{-1}\) and 503.30- 530.93 cm\(^{-1}\), respectively. This experimental result revealed that Al\(^{3+}\), Fe\(^{3+}\) and Cu\(^{2+}\) supressed the recombination rate of photogenerated electrons and holes, hence gave high photocatalytic degradation in methylene blue compared to pure TiO\(_2\). However, Al\(_{1(\text{mmol})}\)-Fe-Cu tridoped TiO\(_2\) solution showed the highest photocatalytic degradation.
5. References

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