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Systematic Study of Calcination Temperature on Photocatalytic Activity of Luminescent Copper(I) Pyrazolate Complex/Titanium Oxide Composites

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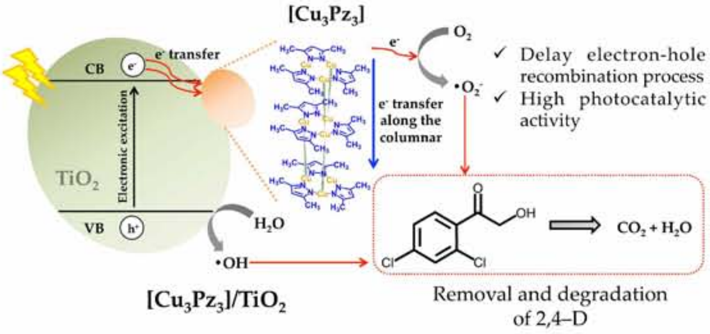
Abstract

Columnar assembly of luminescent 3,5-dimethyl pyrazolate complexes/titanium oxide composites with different metal ions has shown significant improvement in its photocatalytic activity for the removal and degradation of 2, 4-dichlorophenoxyacetic acid (2,4-D). Since photocatalytic activity of semiconductor titanium oxide (TiO_2) with an anatase phase can be improved by calcination temperature, we report the effect of heat treatments on the preparation of copper(I) 3,5-dimethyl pyrazolate complex/titanium oxide composite (**[Cu_3Pz_3]**/TiO_2) for the removal and degradation of 2,4-D. Photocatalyst composites **[Cu_3Pz_3]**/TiO_2 were successfully prepared using an impregnation method with different calcination temperature at 373, 473 and 573 K. Although, the activity of photocatalyst composites **[Cu_3Pz_3]**/TiO_2 was significantly improved with increasing of calcination temperature on pure TiO_2, it was slightly reduced with an increase of calcined temperature to 473 and 573 K. These results showed that **[Cu_3Pz_3]**/TiO_2 was unstable at high temperature due to the decomposition of molecular structure of **[Cu_3Pz_3]** during the preparation of the photocatalyst. Hence, suitable calcination temperature is an important parameter to increase photocatalytic activity of photocatalyst composites **[Cu_3Pz_3]**/TiO_2.

Luminescent composites **[Cu_3Pz_3]**/TiO_2 enable as a semiconductor photocatalyst with a significant improvement on photocatalytic activity for removal and degradation of 2,4-D. This higher photocatalytic activity compared to TiO_2 is due to the presence of columnar assembly for delaying electron-hole recombination between valance and conduction bands. Indeed, calcination temperature is important parameter to increase photocatalytic activity of photocatalyst composites.



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Introduction

Nowadays, an increasing contamination level in water sources with colorless chlorinated compounds is one of the greatest concern to the human future. Since 1945, 2,4-dichlorophenoxyacetic acid (2,4-D) has been widely used as selective herbicides in agriculture fields for controlling the broadleaf weeds [1,2]. In contrast, this herbicide is relatively high soluble in water and easily flow to water stream. In addition, the degradation rate of 2,4-D also considered slow, which takes few days, depending on some factors such as concentration, acidity, and temperature. Several reports showed that 2,4-D in contaminated water source can be removed using chemical, microbial and photochemical process [3-5]. However, those methods still gave low conversion percentage and take a long time for the removal of 2,4-D. Recently, titanium oxide (TiO_2) with its semiconductor properties has been reported as a promising heterogeneous photocatalyst in water treatment technology due to their high activity, large stability, low price, and nontoxic [6-8].

While a lot of strategies have been developed to improve photocatalytic activity of TiO_2 [9-12], modification using copper complexes have gained such a tremendous attention due to the ability of the composite in improving suppression of electron-hole recombination process, in which the columnar structure from a weak metal-metal interaction can trap the transferred electron along its assembly [13,14]. In 2016, a first modified luminescent trinuclear copper(I) pyrazolate complex/titanium oxide has been reported to give better activity compared to pure TiO_2 [13]. This result highlighted that the presence of luminescent trinuclear copper(I) pyrazolate complex (**[Cu_3Pz_3]**) with the different molecular structure of reduced electron-hole recombination process and slightly increased photocatalytic activity of TiO_2. In particular, the luminescent composite of copper complex prepared from 3,5-dimethyl pyrazole ligand with a less rigid molecular structure showed higher photocatalytic activity compared to that 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligand. Recently, we also have reported on photocatalytic activity of modified TiO_2 using 3,5-dimethyl pyrazolate complexes with different group 11 metal ions [14]. Such luminescent properties are required not only for indicating the electron-hole recombination from its emission spectral changes, but also for evaluating the possibility of the electron transfer from conduction band to columnar assembly of the complex.

Although many studies have been done to investigate the performance of pure and modified TiO_2 composites; however, the effect of heat treatment on the activity of luminescent composites has still not yet reported so far. For example, Siah and her co-workers have reported that commercial TiO_2 having anatase phase showed an improvement in the removal and degradation of 2,4-D with increasing of calcination temperature [15]. In contrast, commercial TiO_2 with a combination of anatase and rutile phase possessed different results where the high calcination temperature might change the active site of photocatalyst composites. Therefore, we report on systematic study of luminescent trinuclear copper(I) 3,5-dimethyl pyrazolate complex/titanium oxide photocatalyst composites for the removal and degradation of 2,4-D. In this study, we demonstrated that suitable heat treatment in preparation of TiO_2 composites is also an important parameter to be considered for the improvement of photocatalytic activity.

Experimental Section

Materials and apparatus

Hombikat UV100 TiO_2 (Sachtleben Chemie) was used as a precursor of the anatase phase. **[Cu_3Pz_3]** was previously synthesized from 3,5-dimethyl pyrazole ligand (Sigma-Aldrich, $C_5H_8N_2$ as Pz-CH_3, 99%) and a metal salt of tetrakis(acetonitrile)copper(I) hexafluorophosphate (Sigma-Aldrich, $C_8H_{12}CuF_6N_4P$, 97%) [15,16]. High purity of extra dry tetrahydrofuran, dichloromethane, and methanol from Merck was directly used to synthesize the complex under an inert condition. Freshly distilled triethylamine was firstly prepared in the round bottom flask containing potassium hydroxide (Merck, KOH) under a vacuum and an inert condition using a distillation technique. The freshly distilled triethylamine was directly used for the desired reaction. 2,4-D (Sigma-Aldrich, $C_8H_6Cl_2O_3$, 98%) was used as a model of organic pollutant in the photocatalytic reaction. Calcination with the temperature of 373, 473 and 573 K and a heating rate of 10 K min^{-1} under atmospheric conditions was performed using a Nabertherm muffle furnace on a model of LE6/11.

The structure of the samples was characterized using X-ray Diffractometer (XRD) on a model of Bruker D8 with a scan speed of 0.05 $°s^{-1}$ and Fourier transform infrared spectroscopy (FT-IR) on a model of Nicolet iS50 Thermo Scientific (potassium bromide with a pellet technique). The morphology of the composites was further studied using field-emission scanning electron microscopy (FE-SEM, JEOL on a model of JSM-6701F).

The photocatalytic reaction was performed on UV light irradiation using 200 W Xe-Hg lamp with 8 mW cm^{-2} of light intensity. The photocatalytic activity was evaluated using high-performance liquid chromatography (HPLC) on a model of Shimadzu Prominence LC-20A equipped with UV detector and Hypersil GOLD PFP column (150 x 4.6 mm).

Synthesis of photocatalyst composites

[Cu$_3$Pz$_3$]/TiO$_2$ photocatalyst composites were prepared using an impregnation method where 0.1 weight percent of **[Cu$_3$Pz$_3$]** in dichloromethane solution (25 mL) was mixed with 1.0 g of TiO$_2$. The mixture was sonicated for 20 minutes for better dispersion [13,16,18]. Then, the solution was stirred until dried at room temperature and calcined at 373 K for 4 hours. The protocol was repeated at different calcination temperatures (473 and 573 K) for both unmodified and modified TiO$_2$ to study the effect of heat treatment towards the activity.

Photocatalytic study of photocatalyst composites

[Cu$_3$Pz$_3$]/TiO$_2$ photocatalyst composites were tested for degradation of 2,4-D under UV light irradiation [19,20]. Particularly, photocatalyst composite (50 mg) was added to the solution of 2,4-D (50 mL, 0.5 mM) and stirred in a dark condition for 1 hour to reach the adsorption-desorption equilibrium. Then, the mixture was further stirred for 1 hour under the same UV light irradiation. After the adsorption process and UV lamp exposure, the mixture was collected and purified using a nylon membrane filter (0.2 μm). The filtered solution was further analyzed using HPLC. The concentration of 2,4-D was examined with an eluent mixture of acetonitrile/distilled water in 60:40 (v/v) at wavelength of 283 nm. The removal and degradation of 2,4-D were calculated from equations (1) and (2).

$$\text{Removal of 2,4-D} = \frac{[\text{2,4-D}]_i - [\text{2,4-D}]_f}{[\text{2,4-D}]_i} \text{x}\, 100 \qquad (1)$$

$$\text{Degradation of 2,4-D} = \frac{[\text{2,4-D}]_i - [\text{2,4-D}]_f - [\text{2,4-DCP}]}{[\text{2,4-D}]_i} \text{x}\, 100 \qquad (2)$$

The concentration of 2,4-D before and after UV light irradiation is denoted as [2,4-D]$_i$ and [2,4-D]$_f$ while the concentration of its intermediate (2,4-dichlorophenol, 2,4-DCP) is denoted as [2,4-DCP]. These equations will provide the calibration curves for the determination of photocatalytic activity.

Results and Discussion

Structural analysis of photocatalyst composites

The molecular structure of **[Cu$_3$Pz$_3$]** and **[Cu$_3$Pz$_3$]**/TiO$_2$ photocatalyst composites were firstly confirmed by using FT-IR measurement as shown in Figure 1 [16,21]. According to the previous report, vibration bands at 3375 cm^{-1} (**6**) and 1626 cm^{-1} (**7**) are assigned to O–H group which indicated the presence of moisture. While the vibration band of Ti–O group was observed at the range of 700 to 500 cm^{-1} (**8**) [21]. In contrast, although **[Cu$_3$Pz$_3$]** was prepared as a composite with TiO$_2$, there is no vibration band of **[Cu$_3$Pz$_3$]** in **[Cu$_3$Pz$_3$]**/TiO$_2$ photocatalyst composites due to the low loading amount of the **[Cu$_3$Pz$_3$]**.

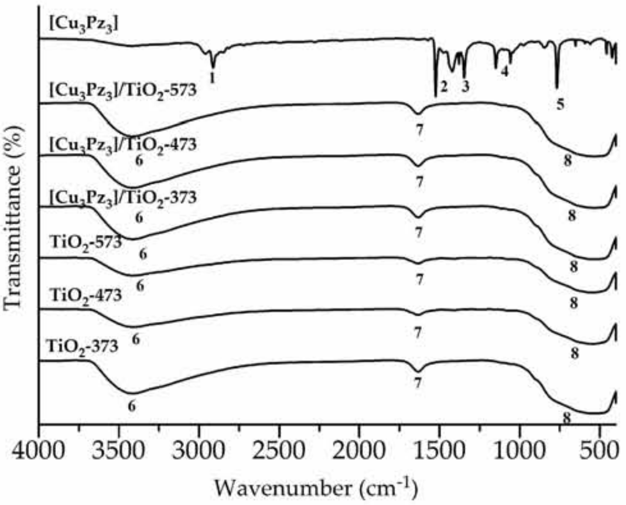

Figure 1. FT-IR spectra of **[Cu$_3$Pz$_3$]** as well as TiO$_2$ and **[Cu$_3$Pz$_3$]**/TiO$_2$ at different calcination temperatures.

Figure 2 shows XRD pattern of TiO$_2$ with 2θ at 25.35°, 38.10°, 48.05°, 54.55° and 62.60° which is related to a standard value of Joint Committee on Powder Diffraction Standards (JCPDS) with the file number of 21-1271. This XRD pattern indicates the presence of an anatase phase for TiO$_2$ [14,20,22]. Moreover, by using Scherrer equation for the main diffraction peak as shown in Table 1, the estimated crystallite sizes of TiO$_2$ and **[Cu$_3$Pz$_3$]**/TiO$_2$ photocatalyst composites were calculated with different calcination temperatures. These results showed that heat treatment slightly affects the crystallite size of pure TiO_2. In contrast, the addition of **[Cu_3Pz_3]** has not affected structural properties of the TiO_2 in its composites. Otherwise, crystallite size of TiO_2 compared to the composites can be used to indicate both the presence of their agglomeration and distribution.

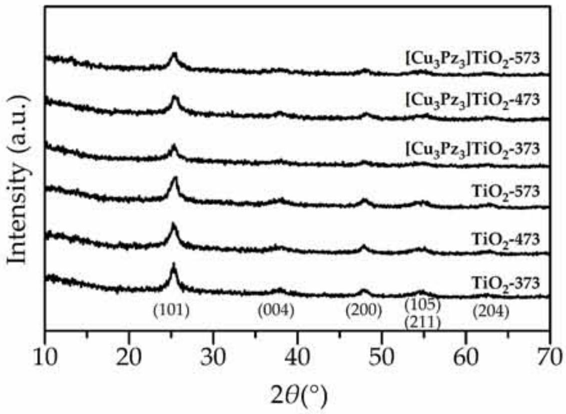

Figure 2. XRD patterns of TiO_2 and **[Cu_3Pz_3]**/TiO_2 at different calcination temperatures.

Table 1. Analyses crystallite size of TiO_2 and **[Cu_3Pz_3]**/TiO_2 at different calcination temperatures.

Photocatalyst composites	Crystallite size[1] (nm)
TiO_2-373	9.5
TiO_2-473	12.3
TiO_2-573	14.8
[Cu_3Pz_3]/TiO_2-373	9.6
[Cu_3Pz_3]/TiO_2-473	9.8
[Cu_3Pz_3]/TiO_2-573	9.7

[1] Calculated using the Scherrer equation.

The morphology of TiO_2 and **[Cu_3Pz_3]**/TiO_2 was studied using FE-SEM measurement. Based on FE-SEM images in Figure 3, the surface morphology of modified **[Cu_3Pz_3]**/TiO_2 photocatalyst composites showed almost similar properties to that of TiO_2. These results showed that **[Cu_3Pz_3]** was dispersed well at the surface of the TiO_2 composites where it was supported by its crystallite size of the composites as shown in Table 1. Moreover, such a small amount of complex will not affect the morphology of the TiO_2 in their composites.

Photocatalytic activity of photocatalyst composites

The performance of TiO_2 and **[Cu_3Pz_3]**/TiO_2 photocatalyst composites was tested at ambient temperature in 1 hour under UV light irradiation. Based on stability test under UV light irradiation with **[Cu_3Pz_3]** only and without photocatalyst, degradation of 2,4-D was not occurred due to lack of hydroxyl radical (•OH^-). By using the equations 1 and 2 for the calibration curve, the performance of photocatalyst composites can be evaluated for percentages of degradation (conversion of 2,4-D to other compounds, except 2,4-DCP) and removal (decreasing of concentration of 2,4-D). the removal can be used for determination of decreasing of concentration of 2,4-D. The photocatalytic testing results of the **[Cu_3Pz_3]**/TiO_2-373 photocatalyst composite (Figure 4) showed that addition of **[Cu_3Pz_3]** was found to give significant highest removal in 96% and degradation in 30% compared to pure TiO_2 (49% and 10%, respectively). Moreover, the photocatalytic activity of pure TiO_2 also showed an improvement with an increase of calcination temperature due to the formation of more anatase phase. This result indicated that the resulting photocatalyst composites might have higher crystallinity of TiO_2 due to the effect of calcination temperature [15].

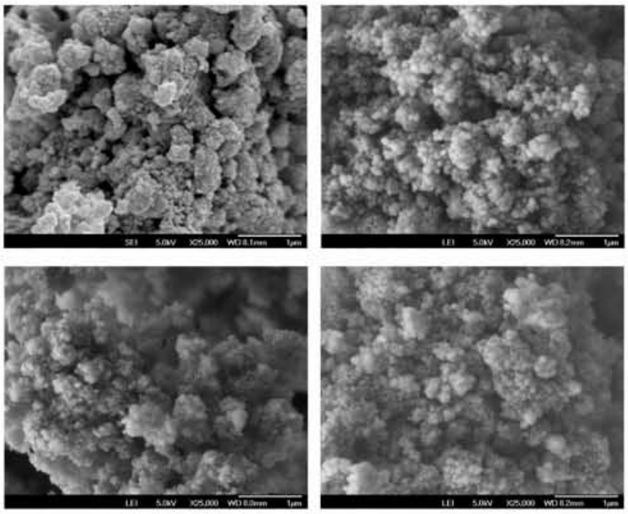

Figure 3. FE-SEM image for the morphology of a) TiO_2 and b-d) **[Cu_3Pz_3]**/TiO_2 at different calcination temperatures of b) 373, c) 473 and d) 573 K.

Based on photocatalytic of TiO_2, it was expected that the composites gave high activity due to the effect of calcination temperature on the crystallinity of TiO_2. Surprisingly, **[Cu_3Pz_3]**/TiO_2 composites showed opposite results where the activity slightly decreased after calcined at 473 and 573 K. These results might be due to the decomposition of **[Cu_3Pz_3]** at high temperature [17]. Hence, presence of **[Cu_3Pz_3]** for delaying electron-hole recombination by trapping the transferred electrons with its columnar assembly [13,14] and suitable calcination temperature [15] play an important role for improving photocatalytic activity of pure TiO_2.

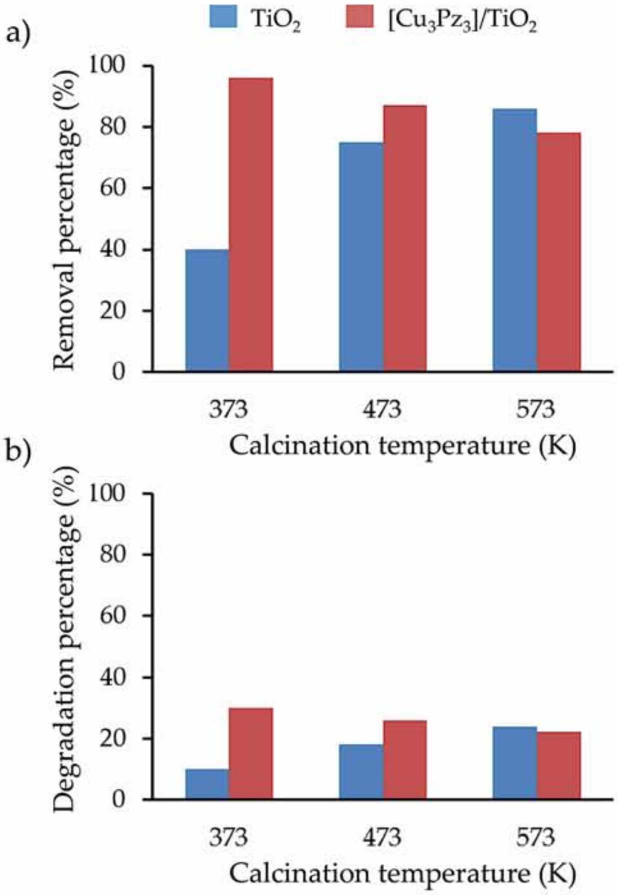

Figure 4. a) Removal and b) degradation percentage of TiO_2 and **$[Cu_3Pz_3]$**/TiO_2 at different calcination temperatures.

Conclusions

In conclusion, TiO_2 and **$[Cu_3Pz_3]$**/TiO_2 photocatalyst composites were successfully prepared at different calcination temperature (373, 473, and 573 K) by using simple an impregnation method. High calcination temperature slightly affects the crystallite size of pure TiO_2. In contrast, the morphology and crystallite size of **$[Cu_3Pz_3]$**/TiO_2 photocatalyst composites were not much affected. Both removal and degradation percentage of 2,4-D for pure TiO_2 increased from 49% to 86% and 10% to 24% when the calcination temperatures were increased from 373 to 473 K and 373 to 573 K. **$[Cu_3Pz_3]$**/TiO_2 photocatalyst composite calcined at 373 K showed the highest removal and degradation of 2,4-D compared to other photocatalyst composites with 96% and 30%. In contrast, as the calcination temperature increased, the activity of **$[Cu_3Pz_3]$**/TiO_2 photocatalyst composites decreased. This work demonstrated that modification of TiO_2 with metal complex and suitable calcination temperature might play an important role to enhance the degradation of organic pollutants.

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