



Synthesis and Application of Cuprous oxide–Potassium Lithium Titanate Composites in the Photocatalytic Degradation of Rhodamine 6G

Areebhorn Baoulan

Department of Chemistry, Faculty of Engineering, Rajamangala University of Technology Isan, Khon Kaen Campus 40000, Thailand

Corresponding author. E-mail address: areeporn.on@rmuti.ac.th

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Abstract

The cuprous oxide–potassium lithium titanate composites were prepared by a conventional solid–liquid reaction between potassium lithium titanate (KTLO) and copper acetate subsequent precipitation with sodium hydroxide and glucose. The cuprous oxide–potassium lithium titanate composites were characterized by X-ray diffraction (XRD), Fourier transforms infrared (FT-IR) spectroscopy and UV-Vis diffuse reflectance spectroscopy (DRS). The photocatalytic activity of the cuprous oxide–potassium lithium titanate composites with different cuprous oxide and potassium lithium titanate loading was evaluated in the photocatalytic degradation of rhodamine 6G under visible light irradiation. The composite which containing lower loading amount of cuprous oxide than potassium lithium titanate showed 82% of photodegradation of rhodamine 6G. The cuprous oxide–potassium lithium titanate composite is eco-friendly material with the performance as photocatalysts under solar light.

Keywords: Composite, Potassium lithium titanate, Cuprous oxide, Photocatalysis, Rhodamine 6G

Introduction

Layered materials based on transition metal oxides have attracted a great deal of attention due to the ion exchange, adsorption and photocatalytic properties (Ide, Sadakane, Sano, & Ogawa, 2014; Ogawa, Saito, & Sohmiya, 2014). The immobilization of functional substance such as noble metal, inorganic semiconductor, and organic dye through intercalation, grafting and adsorption is investigated with the aim of design for the photocatalyst or other functions (Ogawa et al., 2014; Milanović, Sijepović, & Nikolić, 2010; Matsuoka, Ide, & Ogawa, 2014). Among layered transition metal oxides, lepidocrocite-type layered titanates with the general formula of $A_x\text{Ti}_2-y\text{M}_y\text{O}_4$ (A, interlayer cation; M, metal ion or vacancy) have been extensively investigated from the viewpoint of their practical applications in the fields of environment and energy (Ide, Nakasato, & Ogawa, 2010; Ogawa, Morita, Iragashi, & Sato, 2013; Ide, Matsuoka, & Ogawa, 2010). Lepidocrocite-type layered titanate is constituted of edge-shared TiO_6 octahedral. The substitution of lower vacancy metal for Ti site results in the negative charge of titanate sheet which compensating by alkali metal ion such as Rb^+ , K^+ and Cs^+ (Ide et al., 2014). Potassium lithium titanate (abbreviated as KTLO) is a family of the lepidocrocite-type layered titanates consisting of exchangeable ion interlayer K^+ ion. The preparation and application have been reported for such applications as photocatalyst and optical materials (Fuse, Ide, & Ogawa, 2008; Ide & Ogawa, 2007). Previous study has demonstrated that KTLO showed the efficient photocatalytic decomposition of methyl orange by UV irradiation (Ide & Ogawa, 2007), which is a drawback for photocatalysis in the full range of solar irradiation. Therefore, the visible light response of photocatalyst is an important concern for environmental applications. Many efforts have been focused toward designing the visible light photocatalyst by such methods as dye sensitization and heterojunction (Xiong & Zhao, 2014; Li et al., 2004; Xiong, Zhang, Ma, & Zhao, 2010). Xiong and co-worker (Xiong & Zhao, 2014)



demonstrated that the conventional reaction between Cd^{2+} exchanged-layered titanates and sodium sulfide solution presented the *in situ* formation of cadmium sulfide particle in the interlayer space of layered titanate and deposited on the surface of layered titanate with the performance in the degradation of methyl orange under visible irradiation. In addition, the catalyst with a high degradation efficiency and low toxicity may enhance the potential of application in environmental purification.

Recently, much attention has been paid to the use of photocatalytic materials including cuprous oxide (Cu_2O) due to their environment benignity (Huang, Feng, Wang, Yu, & Li, 2009). Cu_2O is a p-type semiconductor with a direct forbidden bandgap of about 2.0–2.3 eV which absorbed the visible light. Many studies have been done to investigate the photocatalytic properties of Cu_2O in treating organic pollutants; however, electron-hole recombination is easy to take place in the particles which reduced the degradation efficiency (Huang et al., 2009). The coupling of Cu_2O with different semiconductors including titanium dioxide (TiO_2) and zinc oxide (ZnO), showed inhibition of the recombination and improve photocatalytic activity (Xiong & Zhao, 2014; Li et al., 2004; Huang et al., 2009). A number of different methods have been practiced to synthesize Cu_2O such as electrochemical and reverse micelle hydrothermal and microemulsion (Dodoo-Arhin, Leoni, Scardi, Garnier, & Mittiga, 2010; Luo, Wang, Yang, Yang, & Chen, 2015; Collisi & Strehblow, 1990). Those methods are inconvenience and complex. In this work the conventional solid-liquid reaction between potassium lithium titanate (KTLO) and copper acetate subsequent precipitation with sodium hydroxide and glucose was investigated to form cuprous oxide-potassium lithium titanate composite. The coupling of Cu_2O with KTLO may inhibited the electron-hole recombination and enhance photocatalytic activity.

Methods and Materials

Materials

Potassium carbonate (K_2CO_3), lithium carbonate (Li_2CO_3) and titanium dioxide (TiO_2) were purchased from Kanto Chemical Co., Ltd. Copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), sodium hydroxide (NaOH) and D-glucose were purchased from Aldrich Co., Ltd. All the reagents were used without further purification.

Sample preparation

The preparation of layered potassium lithium titanate was conducted by a method similar to the previous report (Ogawa et al., 2013). A layered potassium lithium titanate was synthesized by a solid-state reaction among K_2CO_3 , Li_2CO_3 , and TiO_2 . It has been reported that the K_2CO_3 , Li_2CO_3 , and TiO_2 were mixed in the molar ratio of $3x : x : (12-2x)$ to produce the layered potassium lithium titanate with composition of $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ (Sasaki et al., 1998). The starting materials including K_2CO_3 , Li_2CO_3 , and TiO_2 (at the molar ratio of 2.4:0.8:10.4) were mixed manually with an agate mortar and a pestle for 2 h. The mixture was calcined in air at 800 °C for 20 h at the heating rate 10 °Cmin⁻¹. The 32.3 mL of H_2SO_4 (1% mass) was added dropwise to layered potassium lithium titanate slurry at room temperature. The solid was separated by centrifugation (4000 rpm, 20 min), washed with water, and dried under reduced pressure. The product thus obtained was heated at 600 °C for 3 h in air to form layered potassium lithium titanate (KTLO).

The cuprous oxide-potassium lithium titanate (Cu_2O -KTLO) composites were prepared by conventional solid-liquid reaction. $\text{Cu}(\text{CH}_3\text{COO})_2$ was dissolved in absolute ethanol and mixed with the suspension of



KTLO. The mixture was magnetically stirred for 24 hours at room temperature. The mixture was heated to 60 °C under stirring and 25 mL of glucose aqueous solution (0.4 mol/L) was added. Afterward, the mixture was added by NaOH solution (30 mL of 0.3 mol/L) and ultrasonic for 2 min. The mixture was stirred for 30 min at 60 °C and then the mixture was cool to room temperature. The resulting precipitate solid was rinsed with distilled water and pure ethanol to remove CH_3COO^- and the excess amount of glucose and NaOH solution. The products were dried at a temperature of 60 °C for 12 hours. The amounts of $\text{Cu}(\text{CH}_3\text{COO})_2$ and KTLO for the preparation of composites are listed in Table 1. The composites are denoted as Cu_2O -KTLO-1, Cu_2O -KTLO-2 and Cu_2O -KTLO-3.

Table 1 The amounts of $\text{Cu}(\text{CH}_3\text{COO})_2$, and KTLO

Products	$\text{Cu}(\text{CH}_3\text{COO})_2/\text{g}$	KTLO/g
Cu_2O -KTLO-1	0.30	0.30
Cu_2O -KTLO-2	0.30	0.60
Cu_2O -KTLO-3	0.60	0.30

Characterization

Powder X-ray diffraction data were collected on Bruker D8 ADVANCE diffractometer using monochromatic $\text{CuK}\alpha$ radiation. FT-IR spectra were recorded by a Perkin-Elmer Spectrum One Fourier transform-infrared (FT-IR) spectrophotometer by using the KBr pellet method. Diffuse reflectance spectra of the solid sample were recorded with a Shimadzu UV-VIS-NIR-3101PC scanning spectrophotometer using an integrated sphere.

Photocatalytic degradation experiments

Photocatalytic activities of the Cu_2O -KTLO-1, Cu_2O -KTLO-2 and Cu_2O -KTLO-3 were estimated from the change in the concentration of rhodamine 6G at pH 3 under visible light irradiation as a function of time. After the adsorption equilibrium, the irradiation was started until 360 min. The photocatalysis experiments were carried out in a 150 mL glass reactor with 20 mg/L rhodamine 6G aqueous solution and 10 mg of catalyst. The visible radiation source was a Philips 20 W which placed on the top at a distance of 15 cm from the glass reactor. The rhodamine 6G concentration at different intervals of irradiation time was analyzed by UV-Vis spectroscopy at 526 nm.

Results and discussion

After precipitation reaction, the colors of KTLO changed from white to orange for Cu_2O -KTLO-2 and Cu_2O -KTLO-3 (Figure 1d-e) and gray for Cu_2O -KTLO-1 (Figure 1c) and the supernatant liquid were colorless. The Cu_2O solution showed orange color whereas CuO solution revealed green color. This result suggested that the Cu_2O particles were formed in Cu_2O -KTLO-2 and Cu_2O -KTLO-3 composites and the Cu_2O and/or CuO particles were formed in Cu_2O -KTLO-1.

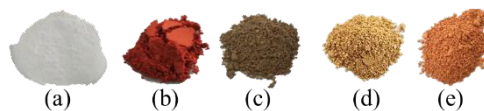


Figure 1 The colors of (a) KTLO, (b) Cu_2O , (c) Cu_2O -KTLO-1, (d) Cu_2O -KTLO-2, (e) Cu_2O -KTLO-3

The X-ray diffraction patterns of KTLO, Cu_2O , Cu_2O -KTLO-1, Cu_2O -KTLO-2 and Cu_2O -KTLO-3 composites are shown in Figure 2. The diffraction peaks of KTLO (Figure 2a) appearing at $2\theta = 11, 29$ and 47° and can be indexed to (020), (130), (200) reflections, respectively, suggesting to the formation of KTLO phase. The assignment the diffraction peaks was in good accordance with the literature data (Fuse et al., 2008). The diffraction peaks of Cu_2O showed at $2\theta = 30, 37$, and 42° (Figure 2b) corresponding to cubic Cu_2O (JCPDS 34-1354). The basal spacing of KTLO increased from 0.77 nm to 0.83 for Cu_2O -KTLO-1 (Figure 2c) and Cu_2O -KTLO-2 (Figure 2d) and 0.98 and 0.83 for Cu_2O -KTLO-3 (Figure 2e) suggesting to successful intercalation of Cu_2O in the interlayer space of KTLO. While the parent KTLO also remained in Cu_2O -KTLO-1 (Figure 2c) and Cu_2O -KTLO-2 (Figure 2d). In addition, the all composites showed diffraction peaks around 30, 37 and 42° , corresponding to the diffraction peaks of cubic Cu_2O . These results showed that when the KTLO dispersion was mixed with copper acetate solution, Cu^{2+} ions replaced K^+ ions via ion exchange process (Ide et al., 2014). The addition of glucose and sodium hydroxide solutions suggested that the *in situ* formation of Cu_2O particles in the interlayer space and spontaneous deposition of Cu_2O on the surface of KTLO were obtained. The average crystalline size of deposited Cu_2O on the surface of KTLO was estimated by using Scherer's equation (Ntwaeaborwa, Mojokeng, Kumar, & Kroon, 2017). The crystallite size of Cu_2O , Cu_2O -KTLO-1, Cu_2O -KTLO-2 and Cu_2O -KTLO-3 were 0.28, 0.15, 0.17 and 0.20 nm, respectively. The crystalline size of Cu_2O was 0.28 nm, which was shown to decrease to 0.15–0.20 nm by the reaction with KTLO.

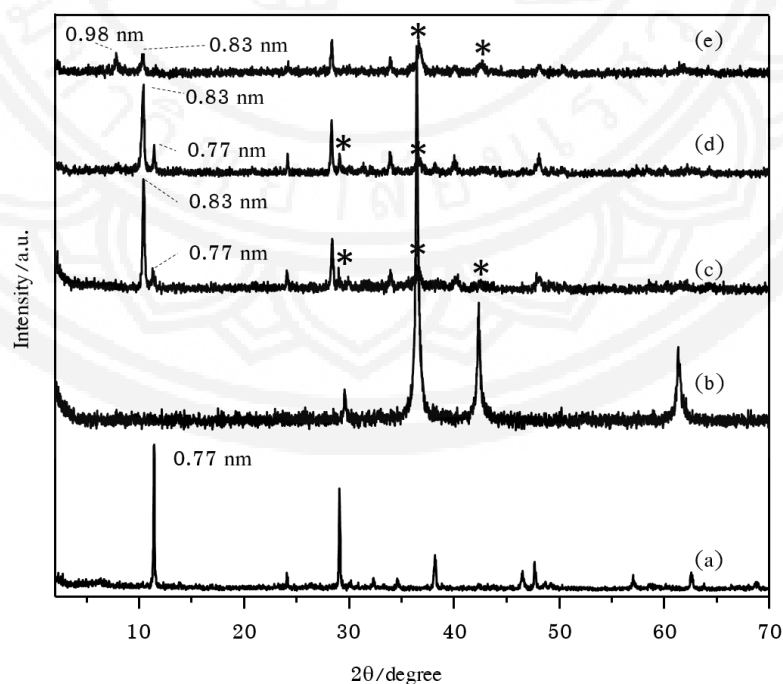


Figure 2 X-ray diffraction patterns of (a) KTLO, (b) Cu_2O , (c) Cu_2O -KTLO-1, (d) Cu_2O -KTLO-2, (e) Cu_2O -KTLO-3

Figure 3 showed the FT-IR spectra of KTLO, Cu_2O , Cu_2O -KTLO-1, Cu_2O -KTLO-2 and Cu_2O -KTLO-3. The FT-IR spectrum of KTLO showed the characteristic bands due to KTLO including a Ti-O stretching, Ti-O- K^+ stretching vibrations at 900 and 520 cm^{-1} (Figure 3a), respectively consistent with the previous report (Milanovic, Stijepovic, & Nikolic, 2010). The FT-IR spectrum of Cu_2O showed that the sharp band peaking at 626 cm^{-1} was due to the stretching vibration of Cu-O (Figure 3b). The FT-IR spectra featured several characteristic bands of KTLO and Cu_2O , in which appeared at 901 , 529 and 630 cm^{-1} for Cu_2O -KTLO-1 (Figure 3c), 900 , 535 and 629 cm^{-1} for Cu_2O -KTLO-2 (Figure 3d) and 900 , 521 and 630 cm^{-1} for Cu_2O -KTLO-3 (Figure 3e). The slightly shifted of the peaks in the composites was due to the interaction Cu_2O and KTLO. These evidences suggested that Cu_2O particles were composited with KTLO.

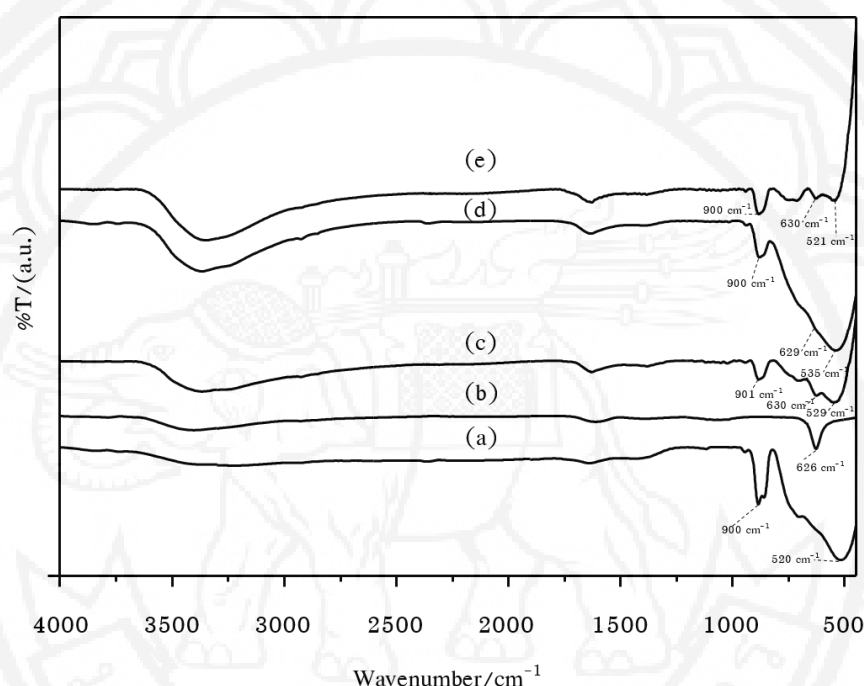


Figure 3 FT-IR spectra of (a) KTLO, (b) Cu_2O , (c) Cu_2O -KTLO-1, (d) Cu_2O -KTLO-2, (e) Cu_2O -KTLO-3

The diffuse reflectance spectra of KTLO, Cu_2O and the composites are shown in Figure 4. The absorption onsets and absorption bands of the composites appeared in the visible region while KTLO revealed at UV region. The absorption onsets of KTLO and Cu_2O were 363 (Figure 4a) and 636 nm (Figure 4b), respectively. It is observed that the absorption onset of KTLO at 363 nm was shifted to higher wavelength after precipitation reaction. The absorption onsets of the Cu_2O -KTLO-1, Cu_2O -KTLO-2 and Cu_2O -KTLO-3 were 725 (Figure 4c), 562 (Figure 4d) and 600 nm (Figure 4e) corresponding to the band gap value about 2.49 , 3.08 and 2.92 eV , respectively. The observation confirmed the presence of Cu_2O in the composites which extended an absorption potential of KTLO in visible region.

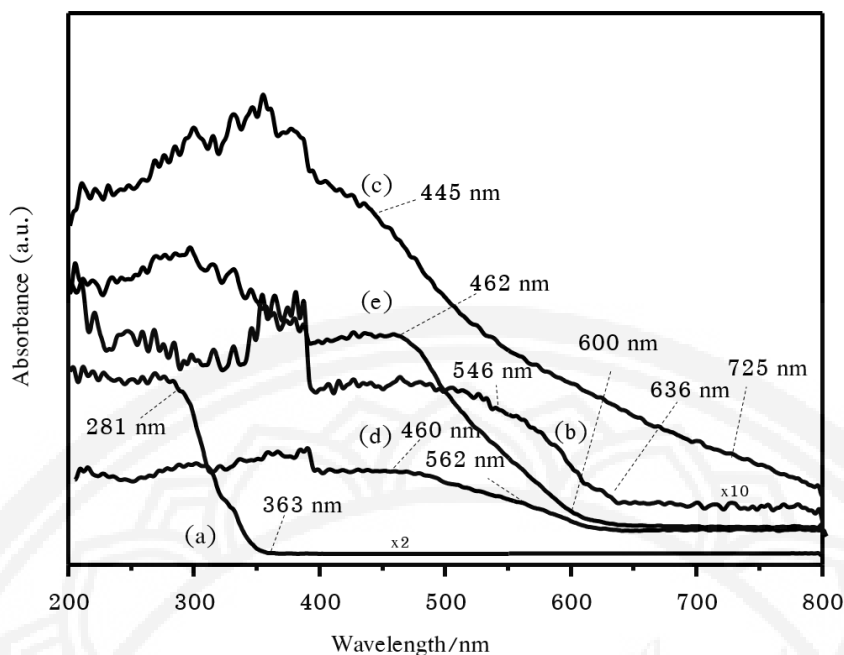


Figure 4 Diffuse reflectance absorption spectra of (a) KTLO, (b) Cu_2O , (c) Cu_2O -KTLO-1, (d) Cu_2O -KTLO-2, (e) Cu_2O -KTLO-3

Figure 5 showed the photocatalytic activity of the Cu_2O -KTLO-1, Cu_2O -KTLO-2, and Cu_2O -KTLO-3 in rhodamine 6G solution at pH 3. Additionally, the photolysis (Figure 5e) and a decomposition experiment in dark environment with catalyst (Figure 5d) were also studied. The small amount adsorption of rhodamine 6G was observed which could be explained by point of zero charge of the composites (ca. 8.2). The surface of the catalyst is positively charge at pH 3. The repulsion of cationic dye (rhodamine 6G) and surface of the catalyst was obtained at pH 3. The degradation efficiency in water purification in the presence of Cu_2O -KTLO-1, Cu_2O -KTLO-2 and Cu_2O -KTLO-3 as catalyst were 56 (Figure 5a), 82 (Figure 5b) and 68% (Figure 5c) after 360 minute of visible irradiation, respectively. The result showed that Cu_2O -KTLO-2 is the superior photocatalyst for the degradation of rhodamine 6G among the three composites. The enhanced activity of Cu_2O -KTLO-2 is probably attributed to the separation of photo-introduced electron-hole pairs in the composite (Huang et al., 2009). The higher amount of KTLO than Cu_2O effected the photocatalyst for the degradation of rhodamine 6G. The reaction rate for the degradation of rhodamine 6G was related to the amounts of KTLO and Cu_2O . An increase in KTLO amount enhanced the reaction rate, in contrast in the case of the Cu_2O .

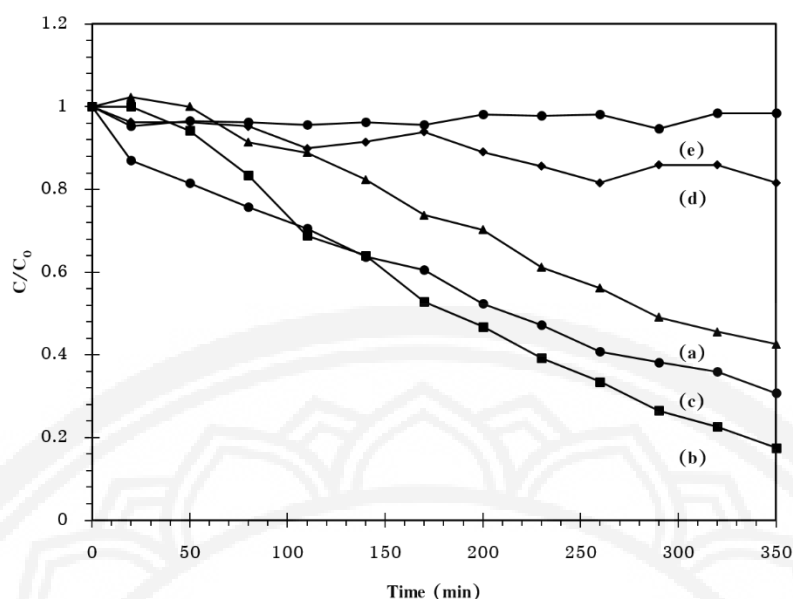


Figure 5 Concentration profiles of rhodamine 6G in the presence of (a) Cu_2O -KTLO-1, (b) Cu_2O -KTLO-2, (c) Cu_2O -KTLO-3 (d) in the dark, (e) absence of a photocatalyst

Conclusion and Suggestions

The cuprous oxide–potassium lithium titanate with different amount of cuprous oxide and potassium lithium titanate was successfully prepared by the conventional solid–liquid reaction and displayed the performance in degrading rhodamine 6G under visible light irradiation.

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