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Hydrothermal Synthesis and Photo Catalytic Properties of Cu3Mo2O9 for the Degradation of Rhodamine B

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ABSTRACT

A Cu3Mo2O9 photo catalyst was successfully prepared by hydrothermal synthesis using ammonium molyb date and cupric nitrate trihydrate as the starting materials. The material thus obtained was characterized by X-ray diffraction, transmission electron microscopy (TEM), as well as ultraviolet–visible (UV-Vis) and Fourier-transform infrared (FTIR) spectroscopy. The photo catalytic activity of Cu3Mo2O9 was evaluated for the degradation of Rhoda mine B (RhB) : the degradation efficiency reaches approximately 89.2% in 60 min at room temperature with an average activation energy of the reaction system is 44.79 kJ·mol¯1, for the reaction system. This result suggested that the Cu3Mo2O9 photo catalyst exhibits excellent absorption and photo catalytic activity for RhB.

Keywords: *Cu3Mo2O9; Photo catalytic activity; Rhoda mine B; Degradation*

INTRODUCTION

With the increase in oil exploration and industrial development, a large number of pollutants have caused serious environmental issue; particularly, wastewater industrial the pollutants causing water pollution have attracted widespread public attention. For solving this serious issue, low cost technology and environment-friendly materials have attractive considerable attention for the purpose of environmental protection [1].

Currently, some of the utilized dyes, such as methylene blue, methyl orange, and Rhoda mine B, are complex; in addition, it is difficult to degrade such organic pollutants; furthermore, a large number of such harmful substances are discharged along with domestic sewage [2]. Moreover, chemical methods for the treatment of pollutants mainly utilize recyclable materials or harmless chemicals; typical treatment methods include coagulation, neutralization, oxidation-reduction, chemical precipitation, electrolysis, adsorption, and ion-exchange [3]. Nevertheless, these chemical methods have some limitations in that secondary pollutants are easily generated. In recent years, photo catalysts exhibiting high activity under visible light have attracted significant interest from several researchers. In this regard, transition metal molybdates such as $AMoO_4$(A=Cu, Ag, Fe) and $B_3MO_2O_9$(B=Cu and Zn) are categorized as metal oxide semiconductor materials; typically, these semiconductor materials exhibit favorable characteristics, such as wide band gap, large specific surface area, and small pore size[4]. In addition, these materials exhibit excellent photo catalytic properties. In this study, a copper molybdate ($Cu_3Mo_2O_9$) photo catalyst was prepared by hydrothermal synthesis method at 190 °C for18 h. The photo catalytic activity of this catalyst was evaluated by the degradation of the RhB under visible light irradiation. The results indicated that $Cu_3Mo_2O_9$ exhibits good photo catalytic efficiency for the removal of organic pollutants.

EXPERIMENTAL

First, 1 mmol of cupric nitrate tri hydrate ($Cu(NO_3)_2.3H_2O$) was dissolved in 25 ml de ionized water, followed by the addition 0.5 mmol of ammonium molybdate ($(NH_4)_5Mo_7O_{24}\cdot 4H_2O$). Second, the solution was stirred 30min, and then it was transferred into Teflon-lined stainless steel autoclaves hydrothermal reactor, which was maintained at 190 °C for 18 h; finally, the sample obtained was washed three times with de ionized water, separated by centrifugation and

dried at 60 °C for 4 h, followed by calcinations at 500 °C for 4 h affording the $Cu_3Mo_2O_9$ photo catalyst .

Characterization

The structure of the photo catalyst was investigated by X-ray diffraction (Bruker D2 Advanced, λCuKα = 1.5418 nm). Transmission electron microscopy (TEM) images were recorded on a Philips CM10 instrument at an accelerating voltage of 200 kV. Ultraviolet-visible (UV-Vis) spectra were obtained on a Hitachi 330 spectrophotometer. The modified sample surface was analyzed by Fourier-transform infrared (FTIR) spectroscopy under the condition of λ = 400 cm^{-1} to 4000 cm^{-1} and at an accuracy of 1cm^{-1}.

Photo catalytic properties

A xenon lamp was used as the light source. The reaction solution was synthesized by the addition of 50 mg of catalyst into 50 mg of RhB solution (7 mg/L). Second, the mixed solution was magnetically stirred in the dark for 30 min for achieving adsorption-desorption equilibrium. The samples were collected at intervals of 10 min between 0 and 60 min under light illumination, centrifugation, and subjected to UV–Vis determination (λ = 550 nm) for determining the absorbance of the supernatant [5]. Simultaneously, a Blank which does not contain the catalyst, and Dark which is not subjected to illumination, containing the same concentration of the RhB solution were used as reference. The photo catalytic degradation rate of the RhB solution was calculated by $\eta = C_o - C_t/C_t \times 100\%$ (η is the degradation rate, Co and Ct are the initial absorbance and instantaneous absorbance of the dye solution at time t after illumination, respectively); hence, the photo catalytic activity is evaluated [6].

RESULT AND DISCUSSION

Fig. 1 shows the phase structure of the sample by X-ray diffraction analysis. The sample was prepared at different temperatures (a) and different times (b). The characteristic peaks of the sample were indexed to the orthorhombic structure of $Cu_3Mo_2O_9$, and diffraction data were consistent with the standard data card for $Cu_3Mo_2O_9$(PDF#70-1495), when the photo catalyst was synthesized at 190 °C for 18 h purity peaks were observed; on the other hand, when the sample was prepared at other temperatures (a) and times (b) impurity peaks were observed, which are indicated by the asterisk in the figure, corresponding to Mo_9O_{25} , Mo_4O_{11} and Mo_5O_{14}, $Mo_{18}O_{52}$ in (a) and (b), respectively. These results recognized that the optimum synthesis condition of obtaining a high purity sample is 190 °C at for 18 h.

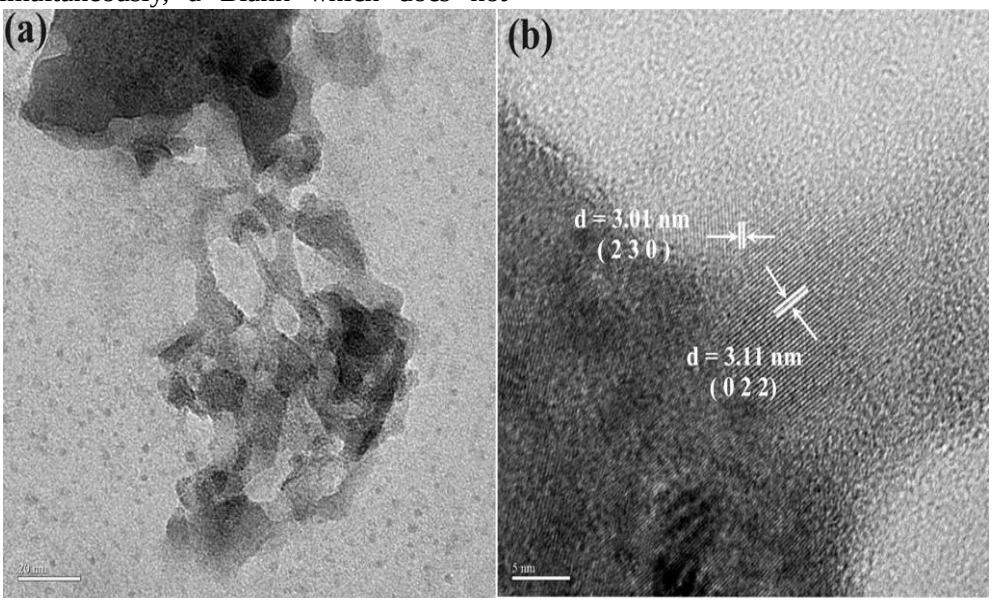

Fig1. *XRD of $Cu_3Mo_2O_9$ (a)different temperatures; (b) different time The TEM image of the sample are shown in Fig. 2, which exhibits the crystalline structure of $Cu_3Mo_2O_9$ synthesized at 190 °C for 18 h. The particles of the $Cu_3Mo_2O_9$ crystal formed aggregates during crystallization, with an average particle diameter of approximately about 10–20 nm. HRTEM images shown that the sample exhibits inter planer spacing of 3.11 nm and 3.01 nm. By the comparison of the standard crystal plane spacing d, characteristic planes for (022) and (230) corresponding to $Cu_3Mo_2O_9$, respectively, were observed* [7].

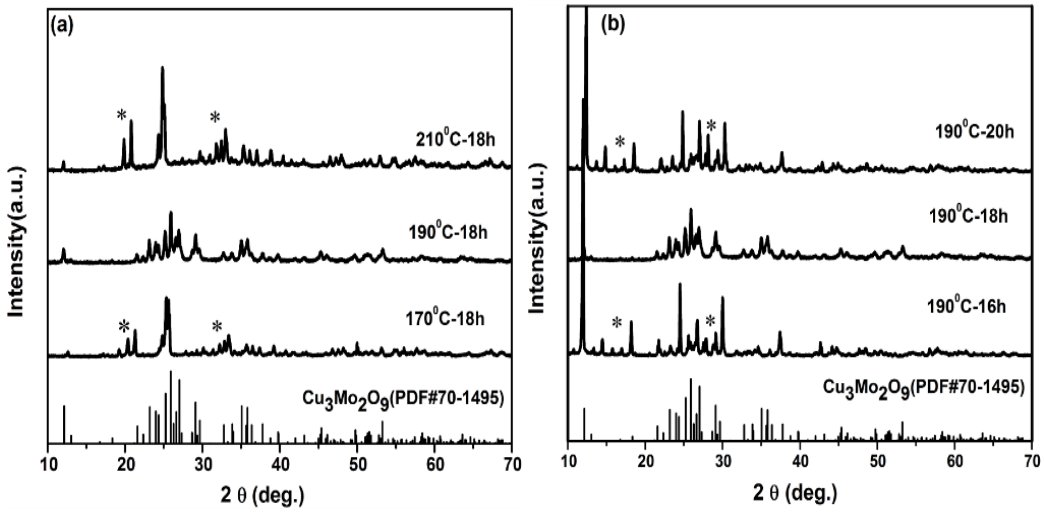

Fig2. *TEM (a) and HRTEM (b). of the sample $Cu_3Mo_2O_9$*

Fig. 3 shows the solid UV–Vis absorption spectra (Fig.3a) of the $Cu_3Mo_2O_9$ photo catalyst and IR spectra (Fig.3b) of the RhB and its degradation products. The optical properties of the material were analyzed by solid ultraviolet diffuse–reflectance spectroscopy. The synthesized sample clearly exhibited light absorption at approximately 460 nm in the visible region, attributed to the transitions of electrons from the valence band to the conduction band. The catalyst characteristic of the catalyst obtained from the UV–Vis absorption spectrum indicated that the band-gap energy can be calculated by $\alpha h\nu = A(h\nu - E_g)^{n/2}$, and the absorption edge of the photo catalyst was 2.7 eV. Results obtained from UV–Vis spectroscopy demonstrate that the $Cu_3Mo_2O_9$ photo catalyst exhibits strong absorption in the ultraviolet and visible–light regions, indicative of enhanced photo catalytic performance [8,9]. Fig.3 (b) shows the IR spectra of the RhB solution at different reaction times. The RhB solution showed a broad peak at 3469 cm^{-1} attributed to the -COOH stretching vibration of RhB. Strong IR absorption bands were observed at 1626 cm^{-1} and 621 cm^{-1} attributed to the -C=N stretching vibration of RhB. In addition, sharp peaks were observed at 1487 cm^{-1}, 1415 cm^{-1}, 1386 cm^{-1}, 1122 cm^{-1} and 1007 cm^{-1} ascribed to the -C=C- , -C=O , -C-CH_3 , Ar-N, and -C-O-C- stretching vibrations of phenol, respectively. Another band was observed at 950 cm^{-1} attributed to the -CH bending vibration. The result obtained from FTIR indicated that the absorption peak of RhB almost disappears with increasing reaction time during degradation, reflective of damage to the RhB benzene ring structure [10, 11].

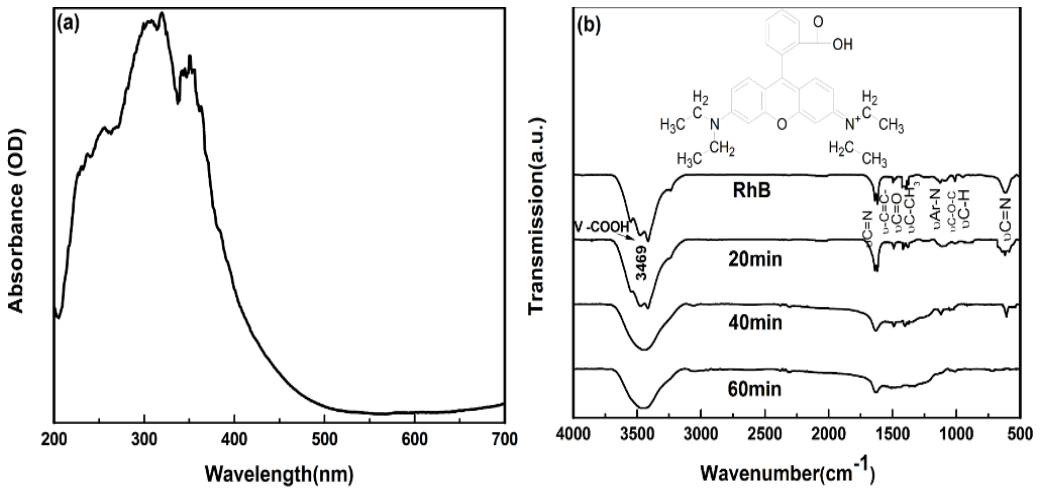

Fig3. *UV-Vis (a) spectra of $Cu_3Mo_2O_9$ and FTIR(b) spectra of the degradation products of RhB at the different times.*

The relationship between the reaction system concentration and illumination time are shown in Fig.4.Fig.4(a) represents that without the catalyst and under black-box conditions only 5.4% of rhodamine B was degraded at a reaction time of 60 min. Hence, the self-

degradation rate of RhB solution is negligible. Photo catalytic experiments were conducted as follows: 50 mg of samples was collected and mixed with 7 mg/L of the RhB solution under different temperature conditions within 60 min for photo catalytic degradation. The results illustrated that with increasing reaction temperature, the photo catalytic activity of the material is enhanced; moreover, at room temperature, the photo catalytic degradation rate was 89.2%, implying that $Cu_3Mo_2O_9$ exhibits high photo catalytic activity. From Fig.4(b) the reaction rate constant, half-life, and average activation energy of the reaction system were obtained and calculated(Table1). The photo catalytic decolonization of RhB can be calculated from the first-order kinetics equation(1), where k represent the apparent rate constant, and C_0 and C_t represents the initial concentration of the RhB solution and that at time t, respectively[12].

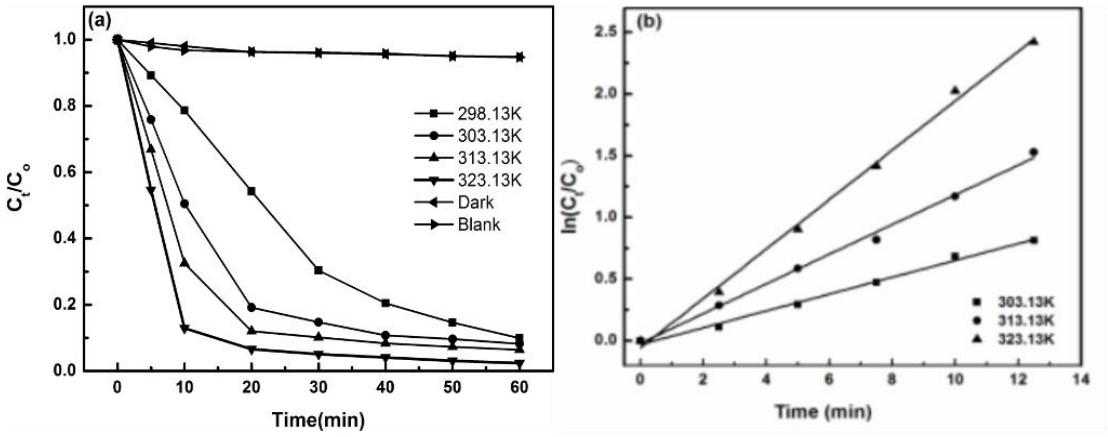

Fig4. *Photo catalytic decolorization kinetics of RhB using $Cu_3Mo_2O_9$ as photocatalyst. The change in reactant concentration versus irradiation time is show as (a) linear and (b) logarithmic plots.*

$$\ln(\frac{C_0}{C_t}) = k_{app}t \quad (1)$$

The activation energy of the reaction system was evaluated at different reaction temperatures by the Arrhenius equation:

$$k = A\exp(-\frac{E_a}{RT}) \quad (2)$$

The obtained equation can be transformed by utilizing T_1 and T_2 as follows:

$$\ln(\frac{k_2}{k_1}) = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \quad (3)$$

With increasing reaction temperature, the reaction rate and half-life of the reaction system were calculated as follows:

$$T_{1/2} = \frac{\ln 2}{k} \quad (4)$$

Where$T_{1/2}$ and E_a represent the half-life and activation energy of the reaction system, respectively.

From equations (2), (3), and (4), k_1 and k_2 represent slopes at different reaction temperatures, and T_1 and T_2 represent the reaction times at different reaction temperatures, respectively. With increasing reaction temperature, the average activation energy of the reaction system was 44.79 kJ.mol^{-1}; in addition, the reaction rate constant increased and the half-life decreased.

Table1.*Rate constants and average activation energy for the photo catalytic degradation of RhB parameters at different reaction temperatures.*

T (K)	Kinetic equation	R^2	k_{app} (min^{-1})	$t_{1/2}$ (min)	$\bar{E}_a$ (kJ/mol)
303.13	$\ln C_T = \ln C_0 - 0.07T + 0.03$	0.992	0.06	10.01	
313.13	$\ln C_T = \ln C_0 - 0.12T + 0.02$	0.994	0.12	5.76	44.79
323.13	$\ln C_T = \ln C_0 - 0.20T + 0.06$	0.995	0.20	3.46	

CONCLUSIONS

The $Cu_3Mo_2O_9$ photo catalyst was prepared by hydrothermal synthesis at different temperatures and different times. The results indicated that

the optimum conditions for the synthesis of the photo catalyst are 190 °C for 18 h. By

Investigating the degradation of RhB, the effects of temperature on the degradation rate and photo catalytic activity of RhB were investigated; at room temperature using the $Cu_3Mo_2O_9$ photo catalyst, the photo catalytic degradation rate was 89.2%, with an average activation energy of 44.79 kJ.mol^{-1} for the reaction system. These result indicated that with increasing reaction temperature, the photo catalytic activity is enhanced, indicating that temperature change exerts a marginal effect on photo catalytic activity. Finally, the photo catalyst exhibits high activity and demonstrates that potential for future applications for the degradation of organic contaminants under visible light.

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