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# Hydrothermal synthesis of $Bi_2MoO_6$ and Its photocatalytic properties in degrading rhodamine B

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## Abstract:

$Bi_2MoO_6$ photocatalyst. can be successfully prepared as the raw of ammonium molybdate and bismuth nitrate pentahydrate by using hydrothermal synthesis method. The obtained materials were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), UV-Vis spectra and Fourier transform infrared(FTIR). The photocatalytic degradation results shows that using the catalyst of synthesized under the condition 200℃ for 12h the degradation efficiency reach about 96.2% in 120 minutes at room temperature and the average activation energy of the reaction system is 30.63 kJ·mol$^{-1}$. The results illustrates that the $Bi_2MoO_6$ photocatalyst have a excellent absorption and photocatalytic activity for Rhodamine B (RhB) solution.

**Keywords:** $Bi_2MoO_6$ ; Hydrothermal synthesis ; Photochemistry; Rhodamine B; Degradation

# 1. Introduction

With the development of industry , a large number of pollutants such as organic and inorganic contaminants have brought serious environmental problems. In this case improvement of photocatalytic activity to solving the energy shortage and environment pollution is an important challenge for photocatalysis materials and technology[1-2]. The molybdates such as $Bi_2MoO_6$, $Bi_2Mo_2O_9$ and $Bi_2Mo_3O_{12}$ etc, which are belongs to the metal oxide semiconductor materials and displays a simple $[(Bi_2O_2)(A_{n-1}B_nO_{3n+1})]$ family of bismuth oxides a layered perovskite structure. Bi containing compounds due to hybridization between Bi6s orbitals and O2p orbitals makes the internal valence band shift up, therefore, most of these materials is photocatalysts capable of responding to visible light [3-4]. These unique physical properties due to this $Bi_2MoO_6$ materials exhibit excellent photocatalysis performance for dye splitting under visible-light irritation, can respond to visible light and ultraviolet light to improve the utilization ratio of sunlight in the degradation of pollutant. However the nanomaterials of inorganic semiconductor is a best direction with to enforce highly active new-generation photocatalysts [5-7].

At present, the preparation method of bismuth molybdate has solid method, molten salt method, ultrasonic reaction method and hydrothermal method[8-9]. Within them, the hydrothermal process is one of the effective method for synthesizing nanostructured $Bi_2MoO_6$ , using this method can be control the shape and size of products by changing the reaction conditions and materials, such as different solvents, reactants, surfactants, reaction temperature and time. Thus, effective synthesis of nano particles with controllable morphology, has significant influence to the properties of the product[10-12].

In this work, a photocatalyst molybdate materials ($Bi_2MoO_6$) were prepared by the hydrothermal synthesis method at different temperature with water and ethylene glycol as solvent. The photocatalytic activities of the sample were estimated by degrading the RhB under the visible light. From the results can be draw the conclusion that the $Bi_2MoO_6$ materials exhibited a good photocatalytic efficiency for organic pollutant.

# 2. Experimental

## 2.1 Synthesis of materials

4 mmol bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$) were dissolved in 25 ml distilled water

and 25 ml ethylene glycol solution, then 0.3mmol ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) into the above solution under the condition of stirring, after the solution stirring 30min, next step solution was transferred into the quartz-sealed hydrothermal reactor and maintained at 180℃, 200℃and 220℃ for 12h, then the sample obtained by washed three times with distilled water, separation by centrifuge and dried at 80℃ for 6h, finally to obtained photocatalyst $Bi_2MoO_6$.

### 2.2 Characteristic

The structure of sample were characterized by X-Ray diffraction (BrukerD2, Cu Kα wavelength is 1.5418 Å). Use of the scanning electron microscope (S-4800, Hitachi) observe the micro morphology of the catalyst. The UV-Vis spectra ware analyzed by Hitachi U-330 spectrophotometer. The surface modification conditions of sample were analysis by FTIR spectrometer (λ=400$cm^{-1}$-4000$cm^{-1}$, accuracy 1$cm^{-1}$).

### 2.3 Photocatalytic properties

The use of xenon lamp as light source, reaction solution were synthesized by 50mg catalyst into 50mg(10mg/L) RhB solution, the mixed solution were magnetically stirring in the dark for 30min to achieve the Adsorption-desorption equilibrium, then samples were taken at every 15min of 120min in the light condition, after centrifugation were using UV-Vis spectrometer(λ=550nm) to determination of the absorbance of supernatant. The photocatalytic degradation rate of the materials for RhB solution was calculate as the formula $\eta = \frac{C_0 - C_t}{C_0} \times 100\%$ (η is the degradation rate, $C_o$ and $C_t$ are initial and after illumination absorbance, respectively) and the photocatalytic activity of the catalyst was evaluated [13-15].

## 3. Result and discussion

The phase structure of the samples were analyzed using XRD, as shown in Fig.1. The sample prepared by 180℃ for 12h (a) , 200℃ for 12h (b) and 220℃ for 12h (c), these characteristic peaks of the sample could be indexed as all diffraction peaks were consistent with the standard orthorhombic structure $Bi_2MoO_6$ crystal diffraction peak (PDF#72-1524), there is no other impurity diffraction peaks. And when the samples prepared under the condition of temperature at 200℃ , the characteristic peaks appear more complete and sharp, compared with the samples prepared under other conditions. Moreover, these sharp and intense peaks

confirmed the existence of highly crystalline nanomaterials.

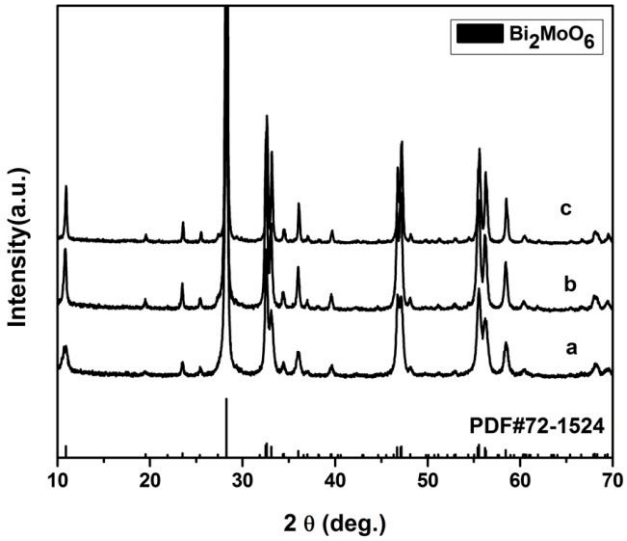


**Fig.1. XRD of $Bi_2MoO_6$ prepared at the different temperature for 12h. (a) 180℃ (b) 200℃ and (c) 220℃**

The SEM images of the $Bi_2MoO_6$ catalyst prepared by hydrothermal method at 12h for different reaction temperature showed in Fig.2. As can be seen from Figure 2 (a), the sample structure was gradually formed to nano particles structure at lower temperature. With an increase in the reaction temperature in the Figure2(c and d) two materials displays a shape of nanoparticles and nanoplates, when the heat temperatures is 200℃ and more than 200℃. in additionally, these nanoparticles has different size and the particle diameter is approximately 50-200nm, the thickness of the nanoplates was about several nm and the average lengths are in extent of 100–300nm. In summary, it can be concluded that the reaction condition is one of the important factors to affect the morphology and the crystallinity of the samples[16-17].

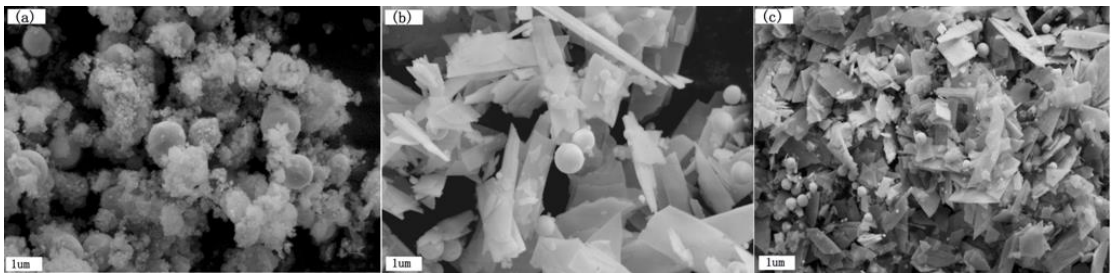


**Fig.2. The SEM of $Bi_2MoO_6$ prepared at the different temperature for 12h. (a) 180℃ (b) 200℃ and (c)220℃**

The IR spectra of RhB solution with different reaction time is showed in Fig.3. The RhB solution showed broad peak at 3469$cm^{-1}$due to -COOH stretching vibration of RhB. The strong IR absorption band at1626$cm^{-1}$ and 621$cm^{-1}$ is attributed to the -C=N stretching

vibration of the RhB. The sharp peaks at 1487cm$^{-1}$, 1415cm$^{-1}$, 1386cm$^{-1}$, 1122cm$^{-1}$ and 1007cm$^{-1}$ are ascribed to the -C=C- , -C=O , -C-$CH_3$ , Ar-N and -C-O-C- stretching vibration of the phenol, respectively. The band at 950cm$^{-1}$ is attributed to the -CH bending vibration. The FTIR result showed that the absorption peak of RhB was almost disappeared with the increasing of reaction time during the degradation process , which can be demonstrated that the RhB benzene ring structure is damaged.

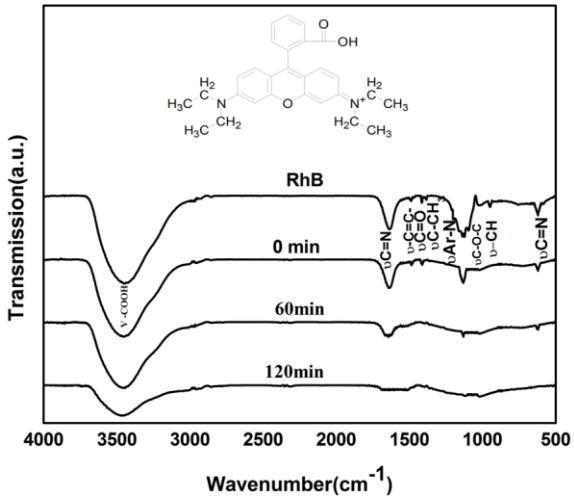


**Fig.3. Infrared spectra of RhB and degradation products.**

The solid UV-Vis absorption spectra of $Bi_2MoO_6$ was showed in Fig.4. The optical properties of the material were analyzed by solid ultraviolet diffuse reflectance spectroscopy. The synthetic samples at about 486.2 nm, 492.9nm and 488.2 nm in the visible region has obvious light absorption, can be seen from the figure that the sample has good absorption in the ultraviolet and visible light , respectively. The catalyst characters of UV-Vis absorption spectrum show that the energy of the band gap can calculated from the equation $\alpha h\nu=A(h\nu-E_g)^{n/2}$ and the absorption edges of the photocatalysts is 2.55eV(a), 2.51eV(b) and 2.53eV(c). The results of UV-Vis demonstrate that the change of synthesis temperature changed the response to visible light, and it is more conducive to the migration of electron hole pair in the catalyst surface under the visible light excitation, which enhances the photocatalytic performance.

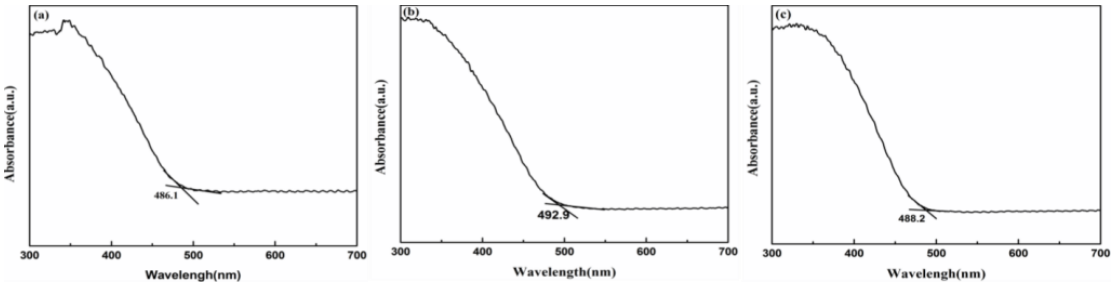


**Fig.4. UV-Vis absorption spectra of the sample ($Bi_2MoO_6$): (a)180 ℃ (b)200 ℃ and (c) 220 ℃-12h**

The relationship between the concentration of the reaction system and the illumination time was expressed by Fig.5. The photocatalytic experiments was as follows: the samples were taken out 50 mg and mixing with the RhB solution 10 mg/L, under the room temperature conditions within in 120min was carried out. The effect of different hydrothermal reaction temperature on the photocatalytic activity of $Bi_2MoO_6$ was investigated by controlling the hydrothermal reaction time(t=12h)，from the photocatalytic degradation curve can be seen, when use the samples of prepared under different conditions, when the hydrothermal temperature increased from 180℃ to 200℃,the photocatalytic activity of $Bi_2MoO_6$ increased gradually with the increase of hydrothermal temperature；When the hydrothermal temperature increased from 200℃ to 220℃, the photocatalytic activity of $Bi_2MoO_6$ decreased with the increase of hydrothermal temperature. When the hydrothermal temperature at 200℃, the photocatalytic activity of the prepared $Bi_2MoO_6$ was relatively highest in 120min, and the degradation rate could reach to 96.2% . The results can be combined with XRD and SEM analysis: when the preparation temperature at 200℃, the diffraction peaks of the samples are the strongest and the crystallinity is the highest, it can be bring about the difference of photocatalytic activity between the sample . Which implied that these catalysts has high photocatalytic activity and the synthesis conditions have an significant influence on the photocatalytic activity of the catalyst.

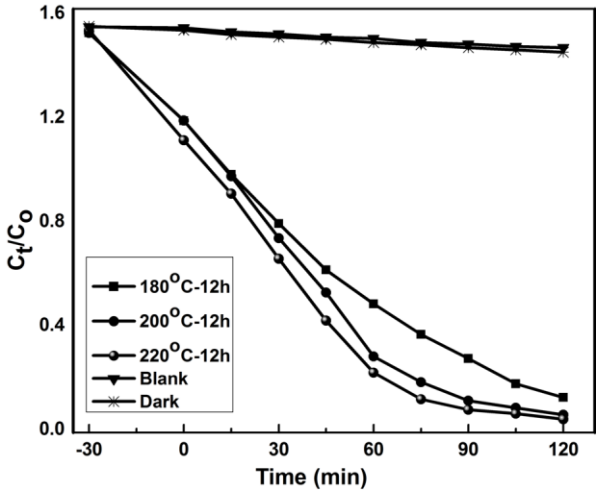


**Fig.5. $Bi_2MoO_6$ as photocatalyst, the photocatalytic degradation of RhB as the dye experimental at the room temperature.**

From the Fig.6(a) can known that under the different temperature with the increase of the reaction temperature the photocatalytic activity of the material was enhanced, this may be due to temperature have influence on the collision and surface migration factors between molecules, and the reaction average activation energy and the half-life with the relational expression between the change of reactant concentration and reaction temperature to explain. From the Fig.6(b) can be obtained the reaction rate constant, half-life and the average activation energy of the reaction system(Table.1). The photocatalytic decolorization of RhB can be calculated from the first-order kinetic equation, in the equation k indicated the apparent rate constant, the $C_0$ and $C_t$ are express the concentration of initial and reaction by RhB solution, respectively.

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

In order to estimate the activation energy of the reaction system at the different reaction temperatures ,according to Arrhenius equation.

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

The obtained equation can be transformed into the following temperature $T_1$ and $T_2$ :

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

By the rising of reaction temperatures, the reaction rate and the half life of the reaction system were calculated by the following formula:

$$t_{1/2} = \frac{\ln 2}{k} \qquad (4)$$

In the (2)(3)(4) equation, the $k_1$,$k_2$ and $T_1$,$T_2$ express the slop and reaction time of the different reaction temperature, respectively. Where $t_{1/2}$ and $E_a$ is half-life and activation energy of the reaction system[18-20].

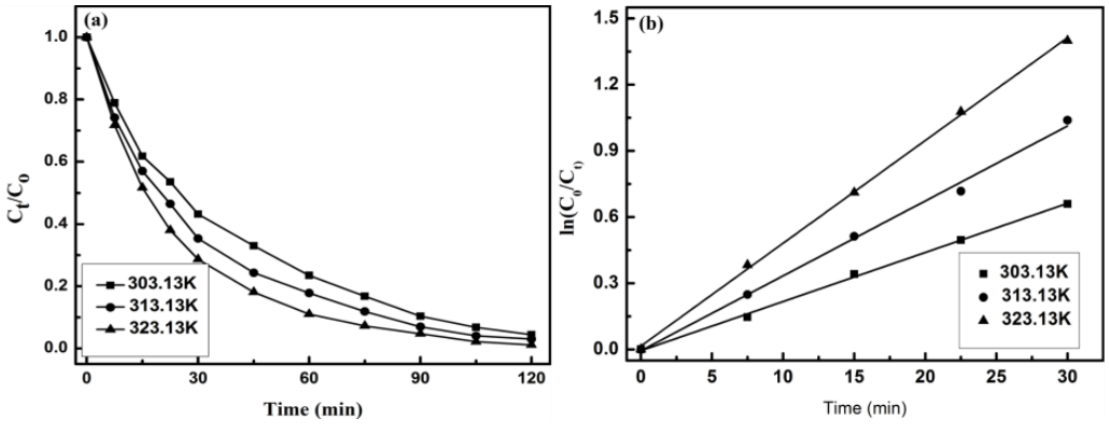


**Fig.6. (a) $Bi_2MoO_6$ prepared at 200℃for 12h as photocatalyst, the photocatalytic degradation of RhB as the dye experimental at the different temperature. (b) Kinetic curve**

It can be calculate that with the increase of reaction temperature the average activation energy of the reaction system is 30.63 kJ·mol$^{-1}$ as well as the reaction rate constant increases and the half-life of the reaction is shortened.

**Table .1 Photocatalytic degradation of RhB parameters under different reaction temperatures**

| Temperature (K) | Kinetic equation | $R^2$ | $k_{app}$ (min$^{-1}$) | $t_{1/2}$ (min) | $\bar{E}_a$ (kJ·mol$^{-1}$) |
|---|---|---|---|---|---|
| 303.13 | $\ln C_t = \ln C_0 - 0.02t - 0.005$ | 0.998 | 0.02 | 34.65 | |
| 313.13 | $\ln C_t = \ln C_0 - 0.03t + 0.006$ | 0.995 | 0.03 | 23.11 | 30.63 |
| 323.13 | $\ln C_t = \ln C_0 - 0.05t + 0.015$ | 0.999 | 0.05 | 13.86 | |

## 4.Conclusions

The photocatalyst $Bi_2MoO_6$ were synthesized by hydrothermal synthesis method at different temperature with water and ethylene glycol as solvent. The results indicates that the synthesis condition of catalyst at the 180℃,200℃ and 220℃ for 12h the $Bi_2MoO_6$ nanomaterials can be synthesized. Using RhB as the degradation object, the effects of temperature on the degradation rate and photocatalytic activity of RhB were studied, at the room temperature use the catalyst($Bi_2MoO_6$) for the photocatalytic degradation rate was 89.5%,96.2% and 95.1%,

respectively, and the average activation energy of the reaction system is 30.63 kJ·mol$^{-1}$. These result shows that with the increase of the reaction temperature the photocatalytic activity was enhanced, indicating that the temperature change has some effect of the photocatalyst activity. Finally, it can be demonstrated that the photocatalyst has a high photocatalyst activity and potential future applications in degradation of organic contaminations under visible light.

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