

Study on synthesis of MoS₂ modified *g*-C₃N₄ materials for treatment of Direct black 38 dye

Nghiên cứu tổng hợp các vật liệu g- C_3N_4 biến tính MoS_2 ứng dụng trong xử lý chất màu direct black-38

Research article

Phung Thi Lan*, Nguyen Thi Kim Giang

Hanoi National University of Education, 136 Xuan Thuy, Cau Giay, Ha Noi, Viet Nam

Pure g-C₃N₄ and MoS₂ modified g-C₃N₄ materials were synthesized using a facile heating method and a low-temperature hydrothermal method, respectively. The obtained samples were characterized by XRD pattern and N₂ adsorption-desorption technique at 77K. The adsorption and photocatalytic performance of all obtained samples were investigated by discoloration of direct black 38 dye in the dark and under visible light irradiation. The results showed that all obtained samples exhibited good discoloration efficiency of direct black 38 dye. The two factors including pH values and Mo loading effected mainly on elimination efficiency of direct black 38 dye. MoS₂ modified g-C₃N₄ materials possessed the more enhanced adsorption and photocatalytic performance in comparison to pure g-C₃N₄ at pH value of 3.5, with adsorbent dosage of 0.1 g/L. Furthermore, it was found that the adsorption process and photo-catalysis simultaneously occurred under visible light irradiation and followed up a pseudo-second-order kinetic reaction of Langmuir - Hinshelwood model.

 $g-C_3N_4$ và $g-C_3N_4$ biến tính bởi MoS_2 đã được tổng hợp theo phương pháp nung đơn giản và phương pháp thủy nhiệt ở nhiệt độ thấp tương ứng. Các mẫu tổng hợp đã được đánh giá đặc trưng bởi các phương pháp hiện đại như giản đồ nhiễu xạ tia X, phương pháp hấp phụ-khử hấp phụ N_2 ở 77K. Khả năng hấp phụ và quang hóa xúc tác của các vật liệu tổng hợp đã được nghiên cứu bởi quá trình phân hủy màu thuốc nhuộm direct black 38 trong điều kiện bóng tối và chiếu sáng bởi ảnh sáng nhìn thẩy của đèn chiếu sáng sợi đốt wolfram (220V-100W). Các kết quả nghiên cứu chỉ ra rằng các mẫu tổng hợp đều có hiệu suất xử lý màu cao đối với thuốc nhuộm direct black 38. Hai yếu tố gồm pH dung dịch và hàm lượng MoS_2 ảnh hưởng chính đến hiệu suất xử lý màu direct black 38. $g-C_3N_4$ biến tính bởi MoS_2 luôn thể hiện hiệu suất hấp phụ và quang hóa cao hơn so với $g-C_3N_4$ tinh khiết. Hơn nữa, khi được chiếu sáng bởi ánh sáng nhìn thấy thì quá trình hấp phụ và quá trình quang hóa thuốc nhuộm direct black 38 trên các vật liệu tổng hợp đã xảy ra đồng thời và mô hình Langmuir - Hinshelwood đông học bâc 2 đã được đề xuất cho quá trình này.

Keywords: adsorption, photo-catalysis, direct black 38, graphitic carbon nitride, molybdenum sulfide

1. Introduction

The economical and efficient uses of catalysts and solar energy for the production of clean energy and environmental treatments attracted attention of various scientists [1 - 3]. A highly efficient, stable, inexpensive, friendly environmental semiconductor material that harvest solar light was also essential for an economical use of catalysts [4]. Recently, graphitic carbon nitride (g- C_3N_4) has been regarded as a good visible-light-driven photocatalyst owing to a suitable band gap to absorb visible light, unique properties and ease of large-scale preparation which were always preferred for practical applications [6, 7]. However, the photocatalytic efficiency of g-C₃N₄ was restricted due to the high rate of recombination of the photo-generated electron-hole pairs, the poor dispersion, easy agglomeration, recycling difficulties. Loading metal oxides on the surface of g-C₃N₄, doping non-metal elements (B, C, S, and N) and combining with proper semiconductors could evidently promote the separation efficiency of photo-induced electron-hole pairs leading to enhance photodegradation

performance [8]. Up to now, g-C₃N₄-based photocatalysts such as $g-C_3N_4/Fe_3O_4$ [9], $g-C_3N_4/Ag_2SO_4$ [10], g- $C_3N_4/Fe_3O_4/Ag_2CrO_4$ [11], g- C_3N_4/CdS -Ag [12], g- C_3N_4/MoS_2 [13-15], $g-C_3N_4/Fe/MoS_2$ [16] were considered as the efficient photocatalysts for degradation of dyes. As an indirect-gap semiconductor, MoS2 had a rather narrow band gap (1.29 eV) in which, its conduction band (CB) and valence band (VB) edge potentials were -0.1 eV and +2.0 eV, respectively. The coupling of g-C₃N₄ with MoS₂ nano-sheets was an ideal construction of heterostructure due to the suitable band-edge positions and good lattice that matched certainly enhancing the ability of visible light harvesting and photo-generated electron-holes separating [13 - 16]. Furthermore, to our best knowledge, the novel investigations for the photocatalytic degradation of direct black 38 dye by pure g-C₃N₄ derived from low-cost urea precursor and MoS₂ modified g-C₃N₄ materials had not been systematically executed to reveal the synergic effect between adsorption progress and photo-catalysis.

In this work, pure g-C₃N₄ were fabricated by a facile heating method derived from low - cost urea precursor and MoS₂ modified g-C₃N₄ materials were synthesized by a low-temperature hydrothermal method. The characteristics of all prepared materials were evaluated by XRD pattern and N₂ adsorption - desorption technique at 77 K. The point of zero charge of MoS₂ modified g-C₃N₄ material was also determined in this study.

The adsorption and photocatalytic performance was investigated by discoloration of direct black 38 dye in the dark and under visible light irradiation. The effect of factors such as pH value, Mo loading and irradiation time were observed. Additionally, the possible degradation kinetic model was proposed.

2. Materials and methods

2.1. Materials

Urea, $(NH_4)_6Mo_7O_{24}\cdot_4H_2O$, $Na_2S\cdot_9H_2O$, hydroxylamine, HCl 35%, KNO₃, HNO₃, NaOH, distilled water and direct black 38 were employed.

Pure $g-C_3N_4$ material was synthesized by directly annealing urea at 550°C for 3 hours. The g-C₃N₄ sample was denoted as CN550. The MoCN550 samples were prepared by hydrothermal method at low temperature [16]. In brief, 1.0 g of g-C₃N₄ was dispersed by sonication in 100 mL of distilled water containing 0.07 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 0.1 g of $Na_2S\cdot 9H_2O$. The mixture was stirred for 2 hours to obtain a homogeneous solution, at which that time, 12 mL of 35% HCl solution was added, and the solution was further incubated at 90°C for 30 min, then 1.0 g of NH₂OH.HCl was added. After that, the solution was maintained at 90°C for further 4 hours to obtain the sample of MoS_2 particles on g-C₃N₄. Finally, the obtained solid was filtered, thoroughly washed with distilled water and dried in an oven at 60°C for 12 hours. The obtained material was donated as 6MoCN550 sample.

For 12MoCN550 sample, the amounts of ammonium molybdate salt, hydroxylamine and sodium sulfide were appropriately changed.

2.2. Methods

2.2.1. Material characteristics

The crystal phase and structure of prepared materials were examined by X-ray diffraction pattern (XRD) and carried out on a Bruker D8 Advance instrument with a X-ray Cu- K_a source at 1.5406 Å.

Batch equilibrium method was used to determine the point of zero charge of 6MoCN550 material by recording the change of pH values of 0.01-M KNO₃ solution after adding exact loading of MoCN550 material. From the obtained results, the plot of initial pH value versus delta pH value was established (*initial pH value was initial pH value of 0.01-M KNO₃ without MoCN550 sample, delta pH value was the minus of final pH value of 0.01-M KNO₃ after adding 6MoCN550 sample). The initial pH values of 0.01-M KNO₃ solution were of 1.4, 3.8, 5.8, 8.1, 10.0 and 11.8. The amount of 6MoCN550 sample was 0.1 g/L.*

The BET surface areas and porous structures of g-C₃N₄based materials were investigated by nitrogen adsorptiondesorption method at 77 K using TRI START 3000 Micromeritics.

2.2.2. Adsorption and photo-catalysis of direct black - 38 over prepared materials

Direct Black 38 (DB 38) (purity of 98%) (tri-azo dye, C.I. number 30235, molecular formula $C_{34}H_{28}N_9O_8S_2Na_2$ and molecular weight of 781.7 g.mol⁻¹) was employed as modelled molecule in our research. The structure of DB 38 is shown in Figure 1.



Figure 1. Structure of direct black 38

For the DB 38 adsorption process, the experiments were carried out by using batch systems at initial dye concentration of 135 mg/L, adsorbent amount of 1.0 g/L and in the dark. The remaining dye concentration was determined by spectrophotometric method (Spectro vision, S6 Biochrom, UK) at $\lambda_{max} = 558.6$ nm. Other factors, such as pH value, MoS₂ contents on g-C₃N₄ material, were investigated to find optimal conditions for DB 38 adsorption in the dark. The adsorption efficiency of DB 38 was determined by the following equation:

$$H = (1 - C/C_0) * 100$$
(1)

where, C_o and C are initial dye concentration and remaining dye concentration of DB 38, respectively. To evaluate the adsorption and photocatalytic performance, the experiments were conducted at optimal adsorption conditions of DB 38 dye but irradiated by visible light of lamp (that made in China, 220V - 100W). The photocatalytic efficiency of DB 38 was also determined by the Equation 1.

3. Results and discussion

3.1. Material characteristic

X - ray diffraction (XRD)

XRD patterns of g-C₃N₄- based materials were shown in Figure 2, where there exited two distinct diffraction peaks. From Figure 2, it could be observed that a strong diffraction peak located at $2\theta = 27.6^{\circ}$ was corresponded to the characteristic interlayer stacking reflection of an aromatic system, denoted as the (002) peak and interlayer

distance of 0.3221 Å. The small diffraction peak around at 13.2° was related to the in-plane structural repeating motif, which was indexed to (100) peak and *d*-spacing interlayer of 6.763 Å [13 - 16].

For MoCN550 materials, the major diffraction peaks coincided well with pure g-C₃N₄. However, no peaks of MoS₂ counterparts were detected by XRD patterns in the 2 θ from 10 - 70°. We believed that this could be attributed to two factors: 1) the loaded MoS₂ was highly dispersed on the surface of g-C₃N₄ and 2) the percentage of MoS₂ was not high enough to detect by XRD pattern. Furthermore, for 6 wt % and 12 wt % MoS₂ samples, there was a light shift in the peak position of g-C₃N₄, indicating a strong interaction exited between MoS₂ species and g-C₃N₄ and the presence of MoS₂ species did not change the nature of g-C₃N₄.



Image: Start Star

Figure 2. XRD patterns of CN550, MoCN550 samples

Point of zero charge of MoCN550

To determine point of zero charge of MoCN550 sample, the plot of initial pH value versus delta pH value was established. The curve of this plot cut the horizontal axis at any pH at which the surface charges of material were zero. The obtained results were shown in Figure 3. From Figure 3, pH 6.9 was considered as the pH value at which the surface charges of MoCN550 sample were zero. At pH lower than 6.9 value, the amine groups on the surface of g-C₃N₄ sample acted as proton acceptors because of the free pair of electrons on the nitrogen atom and became the positive charges (eq. (1), eq. (2). Thus, g-

 C_3N_4 material strongly attracted negative charges in this condition. At pH value higher than 6.9, the amine groups on the surface of g- C_3N_4 reacted hydroxyl ions in aqueous solution (OH⁻), making g- C_3N_4 surface to become negatively charged (eq. (4) and eq. (5)). So that, g- C_3N_4 based material adsorbed well positive charges. The ionization of functional surface groups occurred on the surface of g- C_3N_4 sample as followed:

$$\equiv \mathsf{C}-\mathsf{N}\mathsf{H}_2 + \mathsf{H}^+ \to \equiv \mathsf{C}-\mathsf{N}\mathsf{H}_3^+ \tag{1}$$

$$\stackrel{\equiv C}{=} \stackrel{NH + H^+}{\to} \stackrel{\equiv C}{=} \stackrel{NH_2^+}{\to} (2)$$

$$\equiv C \xrightarrow{NH + OH^{-}} \equiv C \xrightarrow{N^{-} + H_2O} (3)$$

$$\equiv C - NH_2 + H_2O \rightarrow \equiv C - OH + NH_3 \qquad (4)$$

$$\equiv C - OH + OH^{-} \rightarrow \equiv C - O^{-} + H_2 O$$
(5)



Figure 3. The plot of initial pH value *vesus* delta pH value

N_2 adsorption - desorption at 77 K

The N₂ adsorption - desorption method at 77 K was used to investigate specific surface areas, pore volume and pore size of CN550, 6MoCN550 and 12MoCN550 samples. The obtained results were listed in Table 1. The results showed that the BET surface area (S_{BET}) of g-C₃N₄ was found to be quite small, approximately 58.5 m².g⁻¹, of which the micropore surface area (S_{mico}) is also very low, only 2.3 m^2g^{-1} , indicating that g-C₃N₄ material consisted of very small micropores. Therefore, the BET surface area was mainly contributed by the external surface area (S_{ex} = 56.2 m^2g^{-1}). The total pore volume (V_{tot}) was about 0.4711 cm³g⁻¹. Average pore diameter (D) was about 33.66 nm. For 6MoCN550 sample, BET surface area increased lightly, around at 63.2 m²g⁻¹. The increase in external surface area (S_{ex}) contributed to a slight increase of S_{BET} (from 56.2 m².g⁻¹ to 60.4 m².g⁻¹). However, with a slight increase in BET surface area, total pore volume decreased slightly from $0.4711 \text{ cm}^3\text{g}^{-1}$ to $0.4566 \text{ cm}^3.\text{g}^{-1}$ and the average pore diameter decreased from 33.66 nm to 30.13 nm. For 12MoCN550, the factors, such as the decrease in BET surface area, total pore volume, and average pore diameter, were also observed. This meant that some MoS₂ molecules partially covered the pores on the surface of g-C₃N₄ leading to decrease in pore diameter and total pore volume. The higher the MoS₂ content were, the coverage were greater due to the accumulating MoS₂ particles to form larger particles. Although the BET surface area of g-C₃N₄ was found to be quite small, approximately 58.5 m².g⁻¹, the BET surface area of g-C₃N₄ in this work was higher than that of $g-C_3N_4$ published [9, 15, 17, 18].

Samples	S _{BET}	S_{mi}	Sex	V _{mi}	V _{ex}	V _{tot}	D	
	(m^2g^{-1})	(m^2g^{-1})	(m^2g^{-1})	$(cm^{3}g^{-1})$	$(cm^{3}g^{-1})$	$(cm^{3}g^{-1})$	(nm)	
CN550	58.5	2.3	56.2	0.0012	0.4699	0.4711	33.66	
6MoCN550	63.2	2.8	60.4	0.0013	0.4553	0.4566	30.13	
12MoCN550	58.8	-	58.7	-	0.4027	0.4027	27.71	

3.2. Adsorption activity

3.2.1. Effect of MoS₂ loading of MoCN550 samples

The effect of MoS_2 loading on adsorption activity was shown in Figure 4. The experiments were carried out at the pH value of 3.5, initial dye concentration of 135 mg/L, adsorbent dosage of 1.0 g/L and in the dark. The different loadings of MoS_2 were 6 wt% and 12 wt% (calculated theoretically).

As shown in Figure 4, for all obtained samples, adsorption performance enhanced with increasing in adsorption time. After 120 min, adsorption process reached equilibrium state. The adsorption efficiency of MoCN550 materials was higher than that of pure g-C₃N₄ (donated as CN550) during the adsorption time of 240 min and related to MoS₂ amount loaded pure g-C₃N₄. With the increase in MoS₂ loading from 0 to 6 wt%, the

adsorption efficiency extended from 59.4 to 80.3% at the adsorption equilibrium state. However, with further adding MoS_2 amount to 12 wt%, adsorption activity presented a decreasing trend and was around 75.6%.

The specific surface area was one of the factors which affected the adsorption performance. The higher specific surface area was, the better adsorption performance was [17]. The specific surface area of 6MoCN550 was higher than that of 12MoCN550 and CN550 (table 1). Thus, adsorption activity of 6MoCN550 sample was higher than that of 12MoCN550 and CN550 sample. In addition, accumulation of MoS_2 sites at higher loading (12 wt% Mo) could reduce the adsorption efficiency. Herein, the optimal Mo loading in this work was selected as 6 wt% for the next studies.



Figure 4. Effects of MoS₂ loading on adsorption activity of MoCN550

Interestingly, the specific surface area of pure g-C₃N₄ and MoCN550 samples were insignificantly different (table 1) but discoloration efficiency of DB 38 changed clearly between pure g-C₃N₄ and MoCN550 samples. It showed that MoCN550 materials contained two adsorption sites which were MoS₂ site and adsorption sites on the surface of g-C₃N₄.

3.2.2. Effect of pH

It is well known that pH value was considered to be an important factor which influences the adsorption progress. To study the effect of pH values on adsorption efficiency of MoCN550 material, the experiences were conducted by changing pH value from 3.5 to 9.3 and the other conditions were maintained unchanged.

The obtained results were shown in Figure 5. As clearly seen in Figure 5, adsorption activity was enhanced when pH values reduced from 9.3 to 3.5. At the adsorption equilibrium state (after 120 min), adsorption efficiency reached about 80.3%, 73.3%, and 59.4% at different pH value of 3.5, 6.5 and 9.3, respectively. One of the factors used to explain the enhancing in adsorption efficiency of MoCN550 material at different pH values was the point of zero charge of material.

From Figure 3, the point of zero charge of MoCN550 sample corresponded to pH value of 6.9. Therefore, the increase in adsorption efficiency of MoCN550 material at different pH values could be proved that at pH value lower than 6.9, the positive surface charge of MoCN550 sample facilitated to adsorb successfully direct black 38 molecules because these molecules also consisted of amine groups acting as proton acceptors (Figure 1).



Figure 5. Effect of pH value on adsorption activity of 6MoCNN550 sample

3.3. Adsorption and photocalytic activity

3.3.1. Adsorption and photocalytic activity

The adsorption and photocatalytic activity of all prepared materials for degradation of direct black 38 dye under visible light irradiation was evaluated in the experiment conditions such as pH value of 3.5, initial dye concentration of 135 mg/L, material dosage of 1.0 g/L.

Figure 6 displayed the elimination performance of DB 38 dye at different visible light irradiation time. For all obtained samples, discoloration activity strongly increased when visible light irradiation time increased during 150 min. It was observed that the adsorption progress and photo-catalysis simultaneously occurred under visible light irradiation by halogen lamp (220V-100W). Not only MoCN550 sample but also pure g-C₃N₄ sample possessed good adsorption and photocatalytic activity for discoloration DB 38 dye. The enhanced adsorption and photocatalytic performance of MoCN550 materials might be attributed by the synergistic effect between the interface of MoS₂ and g-C₃N₄. In brief, at 150 irradiation time, discoloration efficiencies were 72.5%, 95.9% and 91.5% for CN550, 6MoCN550 and 12MoCN550, respectively. From the obtained results, 6MoCN550 sample exhibited the highest adsorption and photocatalytic activity for discoloration of DB 38. The degradation efficiency was ordered such as 6MoCN550 > 12MoCNN550 > CN550.

Therefore, compared to DB 38 adsorption process in the dark, the simultaneous adsorption and photo-catalysis of all obtained samples exhibited higher efficiency. The adsorption process was found to be an essential factor in photodegradation of the dye. However, because of simultaneous adsorption and photo-catalysis, adsorption efficiency and photocatalytic efficiency could not be distinguished.

It is well known that g-C₃N₄ material could absorb visible light due to narrow band gap energy (E = 2.7 eV) [13 -15]. As irradiated, electrons of valence band of g-C₃N₄

were transferred from valence band to conduction band and left holes. At valence band, these holes can oxidize H_2O to form 'OH radicals. And then, these radicals can continualy oxidize dye molecules. Additionally, photoinduced electrons at conduction band will combined with adsorbed oxygen molecules to produce O2*- radicals which formed 'OH radicals. For MoS₂ and g-C₃N₄ based materials, under visible light irradiation, the photoinduced electrons can easily be transferred from the conduction band of g-C₃N₄ to the conduction band of MoS_2 because the conduction band energy of MoS_2 (CB = -0.12 eV) is lower than that of g-C₃N₄ (CB = -1.22 eV) [13 - 15]. Thus, MoS₂ acts as an acceptor of the photoinduced electrons from g-C₃N₄ and presence of MoS₂ enhance the separation of photoinduce electron-hole pairs. Therefore, the enhanced photocatalytic performation was achieved.



Figure 6. Degradation of DB-38 over all prepared materials at different light irradiation times



Figure 7. Photocatalytic mechanism of MoS_2 -g- C_3N_4 material [15]

From studying on DB 38 adsorption activity, the order of adsorption efficiency was 6MoCN550 > 12MoCNN550 > CN550. This order coincided with the order of DB 38 adsorption and photocatalytic efficiency. It could be seen that there exists synergistic effect of adsorption and photo-catalysis. The adsorption of dye molecules

facilitated their decomposition by photo-catalysis. The more the adsorbed dye molecules were, the more dye molecules were oxidized [19, 20]. The synergic effect could be described as follows [17]: Firstly, dye molecules were adsorbed selectively on the surface of MoCN550 via electrostatic attraction, leading to a higher dye concentration on the surface of MoCN550. Secondly, active species ('OH and 'O₂') generated by photo-catalysis oxidized and decomposed dye molecules on the surface of MoCN550. Finally, the intermediate products were diffused into solution from the surface of MoCN550 materials and a new balance would be established when dye molecules were sequentially adsorbed onto MoCN550 surface (Figure 7).

3.2. Reaction kinetic model

From the obtained results, we concluded that the adsorption and photo-catalysis of direct black 38 simultaneously occurred over MoS_2 and $g-C_3N_4$ based materials under visible light irradiation. MoCN550 materials contained two groups of adsorption sites which were MoS_2 site and adsorption sites on the surface of $g-C_3N_4$. More importantly, according to previous studies [13 - 15], the mechanism of adsorption and photo-catalysis of DB 38 over MoS_2 and $g-C_3N_4$ based materials under visible light irradiation was also reported. Therefore, Langmuir - Hinshelwood kinetic model could be a well description on the catalytic degradation rates of organic compounds [21 - 23]. A simple reaction rate expression is performed with the aid of pseudo-second-order equation [21] as follows:

$$\frac{t}{q_t} = \frac{1}{k_{photo}.q_e^2} + \frac{t}{q_e}$$

Where q_e and q_t are the amount of adsorbed DB 38 over materials after visible-light photocatalyzed per unit mass of sample at steady state and any time t, respectively, while (k_{photo}) is constant value of adsorption and photocatalysis of DB 38.

A linearity plot of t/q_t versus t would determine k_{photo} from the slope and intercept, respectively. As shown in Figure 8, the plots of t/q_t versus irradiation time (t) were linear, which indicate that the degradation of DB 38 went through a pseudo-second-order kinetic reaction. The k_{photo} value, together with the correlation factor (\mathbb{R}^2), are given in Table 2.

Table 2 showed that the rate constant of degradation of DB 38 followed in the order of 6MoCN550 > 12MoCN550 > CN550. This order is quite consistent with the degradation efficiency of DB 38. Thus, increase in reaction rate constant led to increase in the photodegradation efficiency of the as-prepared materials.



Figure 8. The plots of t/qt versus irradiation time, t of all obtained samples

Table 2. k_{photo} value and correlation factor (R²) determined from the pseudo-second-order reaction kinetic model

Samples	k (g.ph ⁻¹ .g ⁻¹)	\mathbf{R}^2
CN550	1.23	0.9958
6MoCN550	1.36	0.9992
12MoCN550	1.32	0.9968

4. Conclusion

Pure g- C_3N_4 and MoS_2 modified g- C_3N_4 materials have been synthesized by a facile heating method and a lowtemperature hydrothermal method. The obtained results showed that pure g- C_3N_4 sample not only has good adsorption performance but also photocatalytic performance for discoloration of direct black 38. Moreover, MoS_2 modified g- C_3N_4 materials exhibited improved adsorption and photocatalytic performance than pure g- C_3N_4 . Among obtained samples, the MoS_2 modified g- C_3N_4 materials with 6 wt% possessed the highest activity for elimination of direct black 38 under in the dark and under visible light irradiation. The photodegradation of direct black 38 under visible light irradiation of all prepared materials followed up a pseudosecond-order kinetic reaction.

5. References

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