Thermodynamic Simulation of Components’ Content in MoS$_2$ Hydrothermal Reaction System and Oxygen–Doped MoS$_2$
One-Step Hydrothermal Preparation Method

Guangtong Zhou$^1$, Hanjian Li$^1$, Xiangbin Zeng$^{2,a,*}$, Wenzhao Wang$^2$, Yishuo Hu$^2$, Shaoxiong Wu$^2$, Yang Zeng$^2$, Guanwei Chen$^2$, Zishen Guo$^2$, Yanhan Liu$^2$ and Haoran Zhang$^2$

$^1$China-EU Institute for Clean and Renewable Energy, Huazhong University of Science and Technology, Wuhan 430074, PR China
$^2$School of Optical and Electronic information, Huazhong University of Science and Technology Wuhan, 430074 PR China
Email: $^a$eexbzeng@163.com

Abstract. Binary nanocomposites of Oxygen-doped molybdenum disulfide was prepared through one-step hydrothermal method. Different effects of initial addition amount of sulfur, hydrazine hydrate and molybdenum oxide on the reaction products were investigated by HCS Chemistry. The direction and process of the hydrothermal reaction were determined by the principle of lowest Gibbs free enthalpy and the components’ content in the reaction system were simulated. Scanning Electron Microscopy (SEM), Raman Spectroscopy (Raman) and X-ray (XRD) was used to characterize the experimental results.

1. Introduction
Transition metal disulfide MS$_2$ (M = Mo, W, Nb, Ta, Ti, Re) is characterized by its unique electrical, magnetic, optical and thermal properties in capacitors, catalysis, lithium batteries, hydrogen storage and evolution, Semiconductor and other fields [1-5]. Among them, molybdenum disulfide (MoS$_2$) is widely used in many fields for its unique atomic structure. MoS$_2$ has a hexagonal crystal lamellar structure, similar to graphene, layers are bounded by van der Waals force, while the layer consisting S-Mo-S three atoms is covalently bonded to form a regular hexagonal structure. Monolayer MoS$_2$ (about 0.7 nm) is a 1.8eV [6, 7] direct bandgap material. Compared with the zero bandgap graphene, molybdenum disulfide has a brighter application prospect in optoelectronic devices, due to adjustable band gap [8-10]; Compared to the three-dimensional bulk structure silicon, molybdenum disulfide can be used to fabricate semiconductors or smaller but more efficient electronic chips, due to the nanoscale two-dimensional film structure [11-16].

In recent years, regulating the carrier type and concentration in the channel of MoS$_2$ through controllable doping, in order to improve the device performance and realize the functional coordination and device integration, has become a new hot spot. Current doping methods can be divided into three kinds: (1) Surface charge transfer [17, 18]: Deposit or adsorb withdrawing/gain electron atoms, small molecules or polymers by the surface charge transfer effect; (2) Element substitution [19, 20]: During or after the growth process, replace molybdenum or sulfur atoms with other atoms; (3) Intercalation [21, 22]: Insert atoms, molecules or ions between layers. More specific, elemental substitution methods can be divided into molybdenum substitution and sulfur substitution. For sulfur substitution methods, Duan [23] et al. used Se to replace part of S and obtained MoS$_2$Se$_2$(1-x)
with band gap differed from 1.85eV to 1.55eV through CVD method, Qin [24] et al. prepared N-doped MoS$_2$ with better catalytic hydrogen evolution capacity through sol-gel method. LAI GuoHong [26] et al. reported that oxygen substitution can effectively increase the light absorption bandwidth, enhance the light absorption properties in UV-Vis light bands, and improve the photoelectric properties of monolayer MoS$_2$, through first principle calculations. However, the controlled oxygen doping method has not been reported till now.

In this paper, the components’ content in the reaction system was simulated with HCS Chemistry, the effects of temperature and reactant compositions were analyzed by thermodynamic methods. Finally, we proposed an one-step hydrothermal preparation method of oxygen-doped MoS$_2$. (HCS Chemistry is a software developed by the United States Outo-kumpu research center for the chemical reaction balance calculation of the integrated thermodynamic, and it is the world’s most widely used chemical thermodynamics calculation software.)

2. Thermodynamic analysis of components’ content in MoS$_2$ hydrothermal reaction system

The Gibbs free energy is a thermodynamic function used to determine the direction of the reaction process. In this paper, we used Molybdenum oxide (MoO$_3$), hydrazine hydrate (N$_2$H$_4$) and sulfur (S) as raw materials and deionized water as solvent. We used the parameters of formulas (1) to (6) and Table 1 to calculate and analyze the possible products of hydrothermal reaction. The minimum Gibbs free energy was used to judge the reaction process of the system.

Hydrothermal reaction can be considered to be at a state with constant temperature, constant pressure and non-volumetric zero. In the formula (1), the $C_{p,m}$ is the molar heat capacity at constant pressure, varies with the temperature, while A, B, C, D is the corresponding coefficient. In Formula (2), the $\Delta_r C_{p,m}$ is the reaction molar heat capacity difference, which can be calculated by summing the product of the reaction stoichiometric coefficients $v$ and all the substance’s molar heat capacity involved in the reaction. Similarly, in formula (3) and (4), the reaction enthalpy $\Delta_r H_m^\theta$ and the reaction entropy $\Delta_r S_m^\theta$ can be calculated. Formula (5) and (6) are used to convert the reaction enthalpy and entropy into those of the hydrothermal reaction temperature. The Gibbs free energy of the reaction can be calculated by the formula (7).

$$C_{p,m} = A + BT + CT^3 + DT^4$$  \hspace{1cm} (1)

$$\Delta_r C_{p,m} = \sum v_B C_{p,m}^B$$  \hspace{1cm} (2)

$$\Delta_r H_m^\theta = \sum v_B H_m^\theta(B)$$  \hspace{1cm} (3)

$$\Delta_r S_m^\theta = \sum v_B S_m^\theta(B)$$  \hspace{1cm} (4)

$$\Delta_r H_m^\theta(T) = \sum \Delta_r H_m^\theta(298.15K) + \int_{298.15K}^{T} \Delta_r C_{p,m} dT$$  \hspace{1cm} (5)

$$\Delta_r S_m^\theta(T) = \sum \Delta_r S_m^\theta(298.15K) + \int_{298.15K}^{T} \frac{\Delta_r C_{p,m}}{T} dT$$  \hspace{1cm} (6)

$$\Delta_r G_m^\theta(T) = \Delta_r H_m^\theta(T) - T\Delta_r S_m^\theta(T)$$  \hspace{1cm} (7)

Theoretically, the reaction equilibrium of MoO$_3$ completely generated to MoS$_2$ by hydrothermal reaction is shown as follows:

$$\text{MoO}_3 + 6\text{N}_2\text{H}_4 + 2\text{S} = \text{MoS}_2 + 3\text{N}_2 + \text{3H}_2\text{O} + 6\text{NH}_3$$  \hspace{1cm} (8)

According to formula (8), we firstly set the initial addition amount of MoO$_3$ as the reaction coefficient, namely 1mol. The reaction temperature was set at 200°C (reported hydrothermal reaction temperature),
the pressure was set as 30bar (standard hydrothermal reaction vessel pressure limit) and the initial amount of deionized water was 10mol (saturated vapor pressure with excess water content), to explore the change rules of reaction products with different initial addition amount of S, N$_2$H$_4$ and MoO$_3$ respectively.

2.1. Effects of initial addition amount of S and N$_2$H$_4$ on hydrothermal products

Sulfur, as a sulfur source for the preparation of MoS$_2$, will only be reduced to S$^{2-}$ in hydrazine hydrate reductive atmosphere theoretically. However, the amount of sulfur added has a great influence on the whole reaction process and the products practically, on the one hand S$^{2-}$ has many compounds, on the other hand there is a competitive relationship between the presence of S as the oxidant and Mo$^{6+}$, so it is very important to study the effects of S.

According to formula (8), we set MoO$_3$ 1mol and N$_2$H$_4$ 6mol as the initial addition amount, the amount of sulfur was increased from 0mol to excess to simulate the components’ content in the hydrothermal reactor. The simulation results are shown in Figure 1.

When sulfur is 0mol, the reaction is:

$$3\text{MoO}_3 + 18\text{N}_2\text{H}_4 (g) = 3\text{MoO}_2 + 7\text{N}_2(g) + 3\text{H}_2\text{O (g)} + 22\text{NH}_3(g)$$

(9)

Here Mo$^{6+}$ is reduced to Mo$^{4+}$, in the form of MoO$_2$, excess N$_2$H$_4$ will conduct its own disproportionation reaction:

$$3\text{N}_2\text{H}_4(g) = \text{N}_2(g) + 4\text{NH}_3(g)$$

(10)

With the increasing amount of S, Mo$^{6+}$ is still reduced to Mo$^{4+}$, while all S is reduced to S$^{2-}$, the product is a mixture of MoO$_2$ and MoS$_2$, until the addition of S reached to 2mol. The reaction occurred at that time is just as it shows in formula (8), all Mo is present in the form of MoS$_2$.

The reaction that occurs in the next stage is based on the reaction of formula (8), only adds the reduction of S by N$_2$H$_4$:

$$\text{N}_2\text{H}_4(g) + 2\text{S} = \text{N}_2(g) + 2\text{H}_2\text{S (g)}$$

(11)

MoS$_2$ maintains to be the vast majority of Mo existence in the reaction system until the S addition amount reaches 10mol. During the process, there is a competition between oxidizing agent: when S increased to 7 ~ 8mol, although oxidizability of Mo$^{6+}$ is stronger than S, but the large presence of S will gradually dominate the competition of reducing agent, so part of the Mo$^{6+}$ is not been reduced and forms as MoS$_3$.

When the addition amount of S reaches 12mol, MoS$_3$ will become the only form of molybdenum in the system. The sulfur element will exhaust all the reduction capacity of hydrazine hydrate, and the final reaction is:

$$\text{MoO}_3 + 6\text{N}_2\text{H}_4(g) + 12\text{S} = 6\text{N}_2(g) + 3\text{H}_2\text{O(g)} + \text{MoS}_3 + 9\text{H}_2\text{S(g)}$$

(12)

![Figure 1. Change of the component content with different amount of S initial addition.](image)
When S is extensively added, the Mo in MoS$_3$ is not in the same valence state as Mo in MoS$_2$. At the same time, MoS$_3$ is not stable and we haven’t find any mature application report, so we have control the addition of S accurately. When S is slightly added, a mixture of MoS$_2$ and MoO$_2$ is formed, which is likely to form oxygen-doped MoS$_2$, but the reducing agent N$_2$H$_4$ plays an extremely important role.

In order to analyze the effect of N$_2$H$_4$, we set the initial addition amount of MoO$_3$ and S as 1mol and 2mol.

![Figure 2](image_url)

**Figure 2.** Components’ quantities versus N$_2$H$_4$ initial addition amount in hydrothermal reaction system at 200°C 300bar, with 1mol MoO$_3$ and 2mol S initially added.

Figure 2 shows the simulation results. It is not difficult to find that N$_2$H$_4$ functioning as reducing agent has an extremely important effect on the composition of the reaction products. When N$_2$H$_4$ is added not that much (less than 1.5mol), the reaction is quite complex. When the amount of hydrazine hydrate is insufficient, MoO$_3$ is partly reduced to MoO$_X$ (X= 2~3), and partly forms as MoS$_2$ and MoS$_3$; S functions as a reducing agent and is partly oxidized to SO$_2$. With the increase of N$_2$H$_4$, the reducing agent S is gradually replaced, and the amount of SO$_2$ decreases rapidly; The morphology of Mo tends to be uniform, high valence state Mo is gradually reduced to lower valence state Mo. However, during this period, the proportion of MoS$_3$ is increased first and then down. It is probably because: although the oxidizability of Mo$_{6+}$ is higher than S, but it is much lower than SO$_2$, N$_2$H$_4$ will try to avoid the oxidation of S, so S will be reduced to S$^{2-}$ as much as possible; However, after the exhaustion of N$_2$H$_4$, the remaining S will still be oxidized by Mo$_{6+}$, but the amount of this part S is very small, so there is more Mo$_{6+}$ in the system in the form of MoS$_3$ than when there is no N$_2$H$_4$ existing, and that is why MoS$_3$ will show an increasing trend; Subsequently, due to the further increase of N$_2$H$_4$, more Mo$_{6+}$ will be reduced to Mo$_{4+}$, so the amount of MoS$_3$ gradually reduces.

In general, Mo$_{6+}$ and S are in a dynamic competitive relationship when hydrazine hydrate is slightly added. Even though the dominant position of the oxidant is occupied at the beginning, the reduction proportion will also be a disadvantage in the competition of reducing agent in the later stage of the reaction.

When the initial addition amount of N$_2$H$_4$ reaches 1.5 mol, Mo and S in the system are reduced to Mo$_{4+}$ and S$^{2-}$, the final molybdenum will all be in the form of MoS$_2$, the reaction is:

$$2MoO_3 + 3N_2H_4(g) + 4S = 2MoS_2 + 3N_2(g) + 6H_2O(g)$$

(13)

While the amount of hydrazine hydrate is further increased, the form of molybdenum and sulfur in the system does not change, the excess N$_2$H$_4$ will occur in the disproportionation reaction, as shown in equation (10).
Finally, we obtain the result that when the initial addition amount MoO$_3$: N$_2$H$_4$: S is 1:1.5:2, the only two reaction products are MoS$_2$ and N$_2$, theoretically; Excess hydrazine hydrate is beneficial to protect MoS$_2$ as the sole product; Appropriate reduction of S addition may form a mixture of MoS$_2$ and MoO$_2$, that is oxygen-doped MoS$_2$.

In this case, we set the initial addition amount of S to 2mol and the initial addition amount of N$_2$H$_4$ is 20mol, considering hydrazine hydrate could be easily decomposed. With the addition amount of MoO$_3$ is gradually increased from 0mol to 2.5mol, the material composition of the system is simulated to verify the preparation method of oxygen doped MoS$_2$.

2.2. Effect of Initial addition of molybdenum on reaction products
As is shown in Figure 3 (NH$_3$ is omitted for the large emission amount), a sufficient addition amount of N$_2$H$_4$ can effectively limit the form of Mo, all the Mo in the system is Mo$^{4+}$. When MoO$_3$ is added in a small amount, it is all in the form of MoS$_2$; When it is initially added in an amount of 1mol or more, extra MoO$_3$ will only generates MoO$_2$ in the reaction system, without any other form of Mo.

The result further confirms previous simulation results in section 1.2. Depending on the results, we propose a one-step hydrothermal method for the preparation of oxygen doped MoS$_2$ by controlling MoO$_3$, N$_2$H$_4$ and S initial addition amount: S added slightly less than 2 times the initial addition amount of MoO$_3$ and keeping N$_2$H$_4$ excessive. In this way, oxygen doped MoS$_2$ was prepared by one-step hydrothermal method without other post processing.

In order to verify the results of simulation, MoO$_3$, N$_2$H$_4$ and S initial addition ratio of the amount of material is 1:20:1.9 was prepared, and select MoO$_3$, N$_2$H$_4$ and S initial addition ratio 1:20:2 as a reference, the oxygen doped MoS$_2$ prepared by one step hydrothermal method was characterized by modern analytical methods.

3. Experiment

3.1. Experimental materials and methods

3.1.1. Preparation of MoO$_3$. 0.75 g of (NH$_4$)$_6$Mo$_7$O$_{24}$ (Aladdin, AR, the ACS, 81-83% AS MoO$_3$) is dispersed in 10ml deionized water and stirred to dissolved, moderate amount of dilute nitric acid is added and thoroughly mixed, then the mixed solution is transferred to a 25 ml polytetrafluoroethylene liner and wrapped in the stainless steel hydrothermal reactor. The mixture was heated at 180°C for 24 h in a blast oven and cooled down under nature conditions, then treated with deionized water and anhydrous Ethanol, washed and centrifuged several times, and finally dried in a vacuum oven at 60°C for 4 h, stored for further using.
3.1.2. Preparation of MoS$_2$ and the Oxygen Doped MoS$_2$. 0.68 g MoO$_3$ prepared by the above method (0.75 g for the oxygen-doped MoS$_2$) mixed with 0.3g S (Medicines, AR, the AR, 99.9%) were dispersed in 5ml hydrazine hydrate (Ji Ning Hongming chemistry, AR, the AR, 80%), then the fully mixed solution was transferred to a 25ml polytetrafluoroethylene liner wrapped in stainless steel hydrothermal reactor. Appropriate amount of deionized water was added until the mixed solution reached 60% of the total volume of the liner, heated at 200°C for 24 h, and then cooled to room temperature.

3.1.3. Characterize the Morphology, Composition and Structure of the Material. Use field emission scanning electron microscope (FE-SEM, HITACHI S-4800, 5.0 kV), laser confocal Raman spectroscopy (Horiba JobinYvon LabRAM HR800 532 nm 200-1100), X-ray diffractometer (XRD, PANalytical PW3040 / 60, voltage 40 kV, current 40 mA, Cu Kα radiation (λ= 1.5406), 2θ=10°~ 80°) to characterize the morphology, composition and crystal structure of samples.

3.2. Experimental results

Figure 4 shows prepared MoS$_2$ and the oxygen-doped MoS$_2$ SEM photographs by hydrothermal method. ((a) MoS$_2$ 20k (b) MoS$_2$ 40k (c) Oxygen doped MoS$_2$ 20k (d) Oxygen doped MoS$_2$ 40k)

Comparing the MoS$_2$ and the oxygen-doped MoS$_2$ SEM images, it can be found that the oxygen-doped MoS$_2$ has a larger agglomerate, the average cluster diameter is 0.1μm, and the size of the extended sheets are relatively short, which is very similar to the structure of MoO$_3$ nanoparticles in reports$^{[25]}$. In MoS$_2$, the average cluster diameter is about 0.5μm, and the sheet is more intensive with some flaky folds on the surface, which indicates that MoS$_2$ is epitaxial grown during the hydrothermal reaction; MoO$_3$ is first reduced to MoO$_2$, and then grow up to form MoS$_2$ flakes on the MoO$_2$ surface. When preparing oxygen-doped MoS$_2$, because of the overdose of the MoO$_3$, the vulcanization reaction of MoO$_3$ is not complete, resulting in larger clusters and shorter elongation.
Figure 5 is MoS$_2$ and oxygen-doped MoS$_2$ Raman spectrures. Figure 5(a) shows that the out-of-plane vibration mode A$_{1g}$ peak of MoS$_2$ located at 403 cm$^{-1}$, while the in-plane vibration mode E$_{2g}$ located at 382 cm$^{-1}$, consistent with the data in the Lloyd Twaites database. Obviously, hydrothermal method can be used to prepare MoS$_2$ with high purity.

\[ \text{Figure 5. Raman spectra of MoS}_2\text{ and oxygen doped MoS}_2\text{ prepared by hydrothermal method. ((a) MoS}_2\text{ (b) Oxygen doped MoS}_2\text{)} \]

Figure 5(b) shows that the out-of-plane vibration mode A$_{1g}$ peak of MoS$_2$ located at 396 cm$^{-1}$, in-plane vibration mode E$_{2g}$ located at 370 cm$^{-1}$, presenting a very obvious redshift. It can be explained by the dielectric limit effect: the increasing Coulomb force between charged particles increases the binding energy and the vibrator intensity between the electrons and holes, which weak the quantum confinement effect and the space confinement, energy change caused by surface effect is greater than that caused by the spatial effect, so that the band gap can be reduced, which leads to spectral redshift. These result is consistent with the simulation of Lai Guohong$^{[27]}$ that the bandgap of MoS$_2$ reduce to 1.4eV from 1.8eV after oxygen doping.

The two absorption peaks of wave number 815 cm$^{-1}$ and 987 cm$^{-1}$ in Figure 5(b) belong to MoO$_3$, probably because the stabilization of MoO$_3$ is better than MoO$_2$. Insufficient vacuum in the vacuum drying process resulted in the oxidation of MoO$_2$, or slow oxidation of MoO$_2$ during storage resulting in the formation of MoO$_3$.

\[ \text{Figure 6. XRD pattern of MoS}_2\text{ and oxygen doped MoS}_2\text{ prepared by hydrothermal method. ((a) MoS}_2\text{ (b) Oxygen doped MoS}_2\text{)} \]

Figure 6 shows the XRD patterns of MoS$_2$ and oxygen doped MoS$_2$. The diffraction peaks of both MoS$_2$ and oxygen doped MoO$_2$ are weak, corresponding to low crystallization degree. The XRD
patterns of MoS₂ are consistent with the standard card (JCPDS 337-1492), which indicates that MoS₂ with hexagonal system was obtained by hydrothermal method. In the XRD pattern of oxygen-doped MoS₂, we can find the two weak peaks near 40° and 65°, which are belonging to <002> and <110> crystallographic orientation of MoO₃ (JCPDS 76-1003).

Through the analysis of experimental results, we can conclude that the feasibility of preparation oxygen-doped MoS₂ by one Step hydrothermal method.

4. Conclusion
HCS Chemistry was used to simulate the effect of sulfur (S) and hydrazine hydrate (N₂H₄) initial addition amount on the hydrothermal products, we found that: with an excess of hydrazine hydrate and slightly less than 2:1 initial addition amount of S:MoO₃, we can get the mixture of MoO₂ and MoS₂. The initial addition amount of molybdenum oxide (MoO₃) is also simulated to verify the results. In turn, we present an one-step hydrothermal preparation method of oxygen-doped MoS₂. By comparing the experimental results of MoS₂ and oxygen doped MoS₂ prepared by hydrothermal method, we verified the feasibility of one-step preparation method and finally we got oxygen-doped MoS₂ with nanostructure clusters.

5. References
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