Application of Hydrothermal and Solvothermal Method in Synthesis of MoS₂

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Abstract: Hydrothermal and solvothermal method were considered as the effective methods for preparation of MoS₂ nanomaterials. The current researches of MoS₂ mainly concerned on electrical properties, the research of reaction system was relatively less. In this paper, synthesis system of MoS₂ was elaborated from precursor, solution, reductant, sulfurizing agent, additive and pH regulator. The application of multifunctional raw materials can greatly simplify reaction system. This provided a reference for the application of hydrothermal and solvothermal method in preparation of MoS₂.

Keywords: hydrothermal, solvothermal, MoS₂, graphene-like structure

1. Introduction

Since the discovery of graphene in 2004 [1], MoS₂ has been widely concerned due to its graphene-like structure [2]. Compared with graphene, MoS₂ is lower cost and considered as an ideal substitute for graphene. MoS₂ is a typical layered material, in the layer is strong covalent bonding of Mo-S, the interaction between layers is Vander Waals forces [3]. As showed in Figure 1, there are three structures for MoS₂ such as 2H(trigonal prismatic), 3R(rhombohedral) and T (trigonal prismatic) [4-6]. For multilayer structure, “Rim-Edge” model is widely accepted [7]. MoS₂ structure with diameter of 3~8nm is nanoctahedra, with diameter of 20~150 nm is polyhedral or nanotubular [8]. Structures with many hundred nanometre is 2H-MoS₂ [9], but 2H-MoS₂ can be converted into 1T-MoS₂ which is driven by the transition metal Mo vacancy [10]. Nowadays, MoS₂ nanomaterials were extensively used in various field such as super dye sensitized solar cell [11], super-capacitor [12,13], hydrogen evolution reaction [14,15], lithium electronic [16,17], sensors [18,19], catalysis [20].

Many methods were developed to prepare MoS₂, such as solvothermal, hydrothermal, template-assisted [21], chemical vapour deposition [22], liquid exfoliation [23], electrochemical anodization [24], insitu-oxidative polymerization [25] and ultrasonication microwave [26]. MoS₂ nanomaterials with different morphologies were synthesized such as nanosphere, nanoflowers, nanowires, nanofibers, nanoparticles and microspheres. The researches of hydrothermal and solvent thermal method focused on the properties and applications of prepared materials. The route and mechanism of design reaction system of hydrothermal and solvothermal method was rarely discussed. The advantages and applications of MoS₂ nanostructured materials in the area of energy and environment were reported [27,28].

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The properties and performances of two-dimensional layered MoS$_2$ in electro-chemical application were covered [29]. In this paper, the design route of hydrothermal and solvothermal method for preparation of MoS$_2$ was studied from six aspects (precursor, solution, reductant, sulfurizing agent, additive and pH regulator), which provided a reference for the application of hydrothermal and solvothermal in future.

2. Materials and methods

For hydrothermal and solvothermal method, teflonlined autoclave was used as reactor, deionized water or organic solvent were used as reaction solvent. Solvothermal method developed on the basis of hydrothermal method, in which deionized water was replaced with organic solvent. These methods were extensively applied to chemical reaction, compound prepared and waste treatment [30-32].

Besides precursor, solution, reductant, sulfurizing agent, additive and pH regulator, temperature is key manipulated factor for reaction process, which can affect the properties and morphology of MoS$_2$ [33]. Only amorphous MoS$_2$ is obtained at 120~150°C [34], with the increasing of reaction temperature, the diameter of products become larger at 230~260°C [35], smaller at 300~375°C [36], monolayer MoS$_2$ is prepared above 400°C [37]. As the reaction temperature goes up, the crystallinity of MoS$_2$ increases and the disorder of material decreases [38]. Besides, high initial temperature also promotes nucleation, thus nuclei aggregation and growth [13], which leads to shorter slabs, more defects and higher catalytic activity.

Compared with solvothermal method, hydrothermal products were poor crystallinity with more defects such as pleats and holes, which were beneficial to electrical and catalytic performance [24,39]. But doping effect of solvothermal method was better. MoS$_2$/RGO hybrid materials prepared by hydrothermal and solvothermal method were contrasted [40], the results showed that MoS$_2$ and graphene were well doped under solvothermal condition. When DMF was replaced with H$_2$O, two separated phases of MoS$_2$ particles and RGO sheets were obtained. Hydrothermal and solvothermal method carried out at low concentrations, morphologies and properties of MoS$_2$ were easy to fabricate. For low yield, the products were rarely used in industrial catalysis, only applied to the study of catalytic mechanism. So, the preparation of MoS$_2$ at high concentration and its application in the field of industrial catalysis may be a hot issue in future.

3. Results and discussions

3.1. Precursor

MoO$_3$, Na$_2$MoO$_4$ [41], H$_2$MoO$_4$, (NH$_4$)$_6$Mo$_7$O$_{24}$, (NH$_4$)$_2$MoS$_4$, Mo(CO)$_6$ and organic precursor were used in the synthesis of MoS$_2$ commonly. Precursors play an important role in the reaction process, different precursors obtain difference composition and morphology. The concentration of precursor affected the morphology of MoS$_2$ crystallites [35]. With the increasing of concentration, the diffusion rate of ions increases, which can decrease the interfacial reaction rate. High concentration impedes the formation of crystal nucleus leading to larger particle size.

Compared with other precursors, (NH$_4$)$_2$MoS$_4$ is special which contains S and Mo element [36, 39, 40, 50, 61, 65]. It can decompose into MoS$_3$ at 573K, and then MoS$_3$ can converted into MoS$_2$ [43,44] at 633K. MoS$_2$ microspheres with uniform morphology were prepared with (NH$_4$)$_2$MoS$_4$ as precursors [50]. Among those precursors, MoO$_3$ was used as bridge to connect other precursors. MoO$_3$ can be easily convert to other precursors such as Na$_2$MoO$_4$, (NH$_4$)$_6$Mo$_7$O$_{24}$, meanwhile other precursors can become MoO$_3$ by high temperature oxidation. MoS$_2$ was prepared by hydrothermal and solvothermal method with MoO$_3$ as precursor, NaSCN as S resource and reducing agent, HCl as pH regulator (Figure 2 a, b). The reaction mechanism was interpreted [43,45] as showed (1,2). Pan [47] prepared MoS$_2$ by solvothermal method with MoO$_3$ as precursor and ethylene glycol as solvent. Among those precursors, MoO$_3$$_2$, Mo$_3$O$_{24}$$_2$ can transform into each other easily in different environments. 3D flower-like MoS$_2$ microspheres (Figure 2 c, d) was synthesized by hydrothermal method with Na$_2$MoO$_4$ as precursor [46] which was comprised by bent sheets with 600nm diameters. Porous MoS$_2$ microspheres were prepared with (NH$_4$)$_6$Mo$_7$O$_{24}$ [48,49]. Compared with inorganic precursor, the reaction temperature of organic
precursor was lower. Hierarchical MoS\textsubscript{2}/Polyaniline Nanowires were prepared by hydrothermal with organic precursor (Mo\textsubscript{3}O\textsubscript{10}(C\textsubscript{6}H\textsubscript{8}N)\textsubscript{2}H\textsubscript{2}O) [51]. Mesostructured lamellar MoS\textsubscript{2} was synthesized mesostructured lamellar MoS\textsubscript{2} with Mo(CO)\textsubscript{6} at 140\textdegree C [42]. New precursor was synthesised through aging, then prepared poor crystalline MoS\textsubscript{2} was obtained by hydrothermal stages, the products displayed excellent hydro-desulphurisation performance [91]. In a word, the species and concentration of precursor have large effects on MoS\textsubscript{2} crystallinity, composition and morphology. Nowadays, it's easy to convert from precursors to MoS\textsubscript{2} but harder to reverse, which limits cyclic utilization of Mo resource. To achieve this process, MoO\textsubscript{3} precursor maybe an appropriate choice.

![Figure 2. a. MoS\textsubscript{2} by hydrothermal with MoO\textsubscript{3} precursor, b. MoS\textsubscript{2} by solvothermal with MoO\textsubscript{3} precursor, c, d. MoS\textsubscript{2} synthesised by hydrothermal with Na\textsubscript{2}MoO\textsubscript{4} as precursor](image)

\[
\begin{align*}
\text{NaSCN} + 2\text{H}_2\text{O} + \text{HCl} & \rightarrow \text{NH}_3 \uparrow + \text{H}_2\text{S} \uparrow + \text{CO}_2 \uparrow + \text{NaCl} \\
4\text{MoO}_3 + 9\text{NaSCN} + 10\text{H}_2\text{O} + 7\text{HCl} & \rightarrow 4\text{MoS}_2 + 9\text{Na}_2\text{SO}_4 + 7\text{NaCl} + 9\text{NH}_3 \uparrow + 9\text{CO}_2 \uparrow
\end{align*}
\]

3.2. Solvent

Deionized water, ethanol, pyrrolidine, N,N-Dimethylformamide (DMF) [40], alkane, N- methyl -2 pyrrolidone (NMP), ethylene glycol [52], n-dodecylamine [53], pyridine [54] and other organic solvents were used as solvent. During the reaction process, the solvent can act as reaction medium and exfoliation agent. The exfoliation effects of nine organic substances were investigated on MoS\textsubscript{2} [55]. The results showed that exfoliation of NMP and cyclohexane was the best and the prepared MoS\textsubscript{2} was 2~5 layers, effects of other solutions were not obvious regularity. Besides, the exfoliation of methanol, ethanol, propyl alcohol and butanol on MoS\textsubscript{2} was studied [57], the rank of denudation ability was methanol < ethanol < propyl alcohol < butanol. Although some solutions no exfoliation ability, their mixed-solvent have certain exfoliation ability. The exfoliation of different concentration of ethanol was investigated [56]. The concentrations of ethanol was 45\%, the exfoliation of MoS\textsubscript{2} was the best, which can be explained by Hansen solubility parameters. The results of the experiment were well in agreement with Hansen solubility parameters [94] (Figure 3a,b). Mixed-solvent molecular size has an important role in the exfoliation attributing to the larger steric repulsion and this phenomenon is elaborated by Leonard-Jones.
NMP and pyrrolidone can induce 1T-MoS\(_2\) to transform into 2H-MoS\(_2\) [58-60]. Unique column-like MoS\(_2\) superstructure composed of edge-terminated MoS\(_2\) nanosheets (CLET MoS\(_2\), Figure 4a, b was synthesised with NMP as solvent and reductant [41]. These structures exhibited excellent electrochemical performance in both lithium ion storage and hydrogen evolution reaction, because CLET MoS\(_2\) exposed more active edges and sites. Pyrrolidone group degraded to produce CO, which improved the purity of MoS\(_2\) for high reducibility of CO [61]. Compared with the hydrothermal method, MoS\(_2\) prepared by solvothermal method was smaller and uniform. Mesostructured lamellar MoS\(_2\) was obtained with n-dodecylamine as the medium [42]. MoS\(_2\) nanoflowers decorated reduced graphene oxide paper were prepared with DMF as solvent [62].

There are two theories were applied to select solution such as Young’s equation (3) and Hansen solubility parameters [63]. Young’s equation involves solid-liquid, solid-gas, liquid-gas surface tension, this method reflects the influence of solution through angle of interfacial tension. Young’s equation can be applied to forecast the optimal co-solvent concentration of exfoliation [57]. Hansen solubility parameters combined the effects of dispersion forces, dipole-permanent dipole and hydrogen bonding forces. Hasan solubility parameter can be used in solvent prediction [64, 65], the results were coincident with the experimental results. Hansen solubility parameters was suitable for pure solvent and mixed solvent (5). Hansen solubility parameters was applied to predict the exfoliation of layered compounds in different concentration of ethanol [56]. Besides, steric effect, boiling point and molecular weight should be taken into account when select the reaction solution. So, liquid paraffin, diphenyl ether, oleamine, oleic acid, other high molecular weight and high boiling point alkane solvents also are good potential solution.

\[
\gamma_{sl} = \gamma_{lg} - \gamma_{lg} \cos \theta_c
\]

\[
R_a = \left[4\left(\delta_{D,sl} - \delta_{D,soh}\right)^2 + \left(\delta_{P,sl} - \delta_{P,soh}\right)^2 + \left(\delta_{H,sl} - \delta_{H,soh}\right)^2\right]^{0.5}
\]
\[ \delta_{\text{blend}} = \sum \phi_{n,\text{comp}} \delta_{n,\text{comp}} \]  

(5)

\( \gamma_{sl}, \gamma_{sg}, \gamma_{lg}, \theta_c \), which are the solid–liquid, solid-gas, liquid-gas interfacial energy, and equilibrium contact angle. \( R_a, \delta_D, \delta_p, \delta_H, \Phi \), which are HSP distance, dispersive, polar, and hydrogen-bonding solubility parameters, volume fraction for each composition.

3.3. Reductant

The reductant can reduce \( \text{Mo}^{6+} \) to \( \text{Mo}^{4+} \), so the addition of reductant can improve the crystallinity of \( \text{MoS}_2 \). The application of reductant reduce the reaction temperature. Generally, water soluble reductants were used in the hydrothermal method, the oil soluble reductants were applied in solvothermal method.

Generally, reductant contains reductive functional groups such as –OH, –C=O, –C=C–, –NH₂, \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O}, \text{NH}_2\text{OH}\cdot\text{HCl} \) [34,66], ethylene glycol and \( \text{NH}_2\text{OH}\cdot\text{H}_2\text{SO}_4 \) [67] were widely used. Among these reductant \( \text{NH}_2\text{OH}\cdot\text{HCl} \) is special and oxidation product is \( \text{N}_2 \), which does not coat the active site. \( \text{MoS}_2 \) was synthesized with \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) as reductant at different temperatures, the mechanism of reaction was illustrated (6,7) [68,69]. Flower-like \( \text{MoS}_2 \) was prepared with \( \text{NH}_2\text{OH}\cdot\text{HCl} \) as reducing agent at assistance of ionic solution (Figure 5), the mechanism of which was stated (8) [50].

The species of reductant have different influence on the chemical composition of products. Chemical composition of prepared \( \text{MoS}_2 \) was studied with various reductant [53]. When the reductants were \( \text{N}_2\text{H}_4, \text{NH}_2\text{OH}, \text{N}_2\text{H}_4\cdot\text{NR}_4\text{Cl}, \text{NH}_2\text{OH}\cdot\text{NR}_4\text{Cl} \), the products were \( \text{MoS}_{2.4}, \text{MoS}_{3.05}, \text{MoS}_{2.1}\text{C}_{1.58}, \text{MoS}_{2.19}\text{C}_{1.62} \). Small molecule reductants were widely used, the applications of macromolecular reductants were relatively less. Compared with small molecule reductant, there are two advantages for macromolecular reductant. On the one hand, the reducibility of macromolecule reductants is more stable, on the other hand, macromolecule reductants play a role of coating which can affect the morphology of reaction products. Reductants for hydrothermal and solvothermal method are relatively less, reducing agents for other transition metal materials deserve to study and advocate. For example, \( \text{H}_2 \) [70], lithium borohydride [71], \( 1\)-\( \text{octadecene} \) [72], \( 1,2\)-\( \text{dodecanediol} \) [73], ascorbic acid [74].

![Figure 5. SEM of microspheres](image_url)

3.4. Additive

Macromolecular surfactant and inorganic salt were used as additives. Surfactants served as template and anchor, which controlled the morphology of the products. Additives improved the dispersion of precursor in solution by creating microenvironment, which increased the dispersion of products [75]. Additives affected interfacial reactions by adjusting interfacial tension. PEG, PVP, P123, SDS, CTAC, AOT, CTAB [65], ionic liquid, \( \text{C}_{10}\text{H}_{36}\text{BrN} \), TOP and compounds with large molecules and high boiling points were widely used. The effects of PEG, P123, SDS, AOT and CTAB on product morphology were
investigated by hydrothermal method [69] (Figure 6a~f), the results showed that various surfactants led to different morphologies. MoS₂ microspheres were synthesized with C₁₆H₃₆BrN as additive, the mechanism was elucidated (Figure 7a) [45]. After adding C₁₆H₃₆BrN, the surface of microspheres became smoother. The application of additives was favourable to fixation and nucleation, MoS₂/Fe₃S₄, CoMoS/Fe₃S₄, NiMoS/Fe₃S₄ and MoS₂/SiO₂/Fe₃O₄ with CTAB and SDS were synthesized as additives [76,77]. The application of additive make the morphology of products become more homogeneous. uniform C@MoS₂ was prepared PVP as additive and carbon source [78]. Flower-like MoS₂ was prepared with TOP as additive and MoS₂ NFs composed of crumpled MoS₂ NSs with more active edges [62]. Ionic liquid also played a crucial role in the formation of MoS₂ microspheres.

With adding ionic liquid, ion-covered vesicles can be formed, which provide nucleation domains for the hydrothermal reaction. MoS₂ nanosheets grew larger, stacked together and curled on the vesicle surfaces during hydrothermal process, resulting in the formation of MoS₂ microspheres. The mechanism of the MoS₂ microspheres with ionic liquid was illustrated (Figure 7b). Without ionic liquid the structure of products changed obviously [50,79] (the peak of (002) became weaker). Inorganic salts affected the structures and properties of product through synergistic effect and shielding effect. The effects of CH₃COONa and NH₄Cl on the synthesis of MoS₂ was investigated [35]. CH₃COONa and NH₄Cl can inhibit the formation of MoS₂ crystal nucleus at interface, which increase the particle size of product. Wu [80] deemed that the introduction of NH₄⁺ can improve the ability in the electrical conductivity. Nowadays, the application of additives mainly concentrated on macromolecular surfactants, the research on inorganic salts was rare. The effects of inorganic salt on the products need to be investigated further.

![Figure 6. SEM images of MoS₂ samples synthesized with different surfactants.](image)

![Figure 7. Formation mechanism of the MoS₂ microspheres with additive.](image)

3.5. Sulfurizing agent

In the preparation process, the sulfurizing agent acts as a sulfur source, some sulfurizing agent acts as a reductant agent. Thiourea, cysteine, elemental sulfur [42,54], sodium sulfide [34], NaSCN, (NH₄)₂S, CS₂ [81], H₂S, DMDS (Methyl disulfide) [81], thiglycolic acid [93], thioacetamide [69,78,79] were used. Functionally, sulfurizing agents can be divided into two types, one is directly provideS S²⁻, such
as Na$_2$S, (NH$_4$)$_2$S, the other is the decomposition to produce H$_2$S, such as thiourea, cysteine, thioacetamide. When the former is used as sulfurizing agents, the reaction temperature is higher. Only H$_2$S and S elemental were used as sulfurizing agents, the products were MoS$_2$ [39]. High activity MoS$_2$ nanocatalyst was prepared with Na$_2$S as sulfurizing agent [33]. Besides, sulfurizing agents also affected the morphology of product. Spherical MoS$_2$ nanocrystals can be obtained with L-cysteine, MoS$_2$ nanosheets were formed with thiourea [82]. Mo/S can influence the chemical compositions of product. The effects of Mo/S were studied [54] under solvothermal condition. When Mo/S was 0, 1:1, 1:2, 1:3, the reaction products were MoO$_2$, MoO$_3$ and MoS$_2$, MoS$_2$, MoS$_2$ respectively. Polysulfide compounds on poor crystallinity MoS$_2$ surfaces was observed [83]. Excessive thiourea adhered to the surface of the crystal and affected further growth of crystal [84] (Figure 8). The mechanism was expounded [68] (9~10), and different mechanisms were proposed [85]. Nowadays, the applications of macromolecule sulfurizing agent were less. Compared with small molecule sulfurizing agent, macromolecule sulfurizing agents play a certain role in coating. Smaller particles and uniform product can be synthesized with macromolecule sulfurizing agent. Nanocrystals with a diameter of 10nm was prepared with bis (trimethylsilyl) sulfide (TMS) [72] as sulfurizing agent.

![Figure 8. Route of thiourea function](image)

3.6. pH regulator

The acidic environment plays an important role in preparation of MoS$_2$ [86], which can accelerate rate crystallization [87] through adjusting the consumption of H$^+$ [88, 92]. Park believed that H$^+$ catalyzed hydrothermal reaction process [82]. The concentration of H$^+$ also affects the existence state of precursors [89, 92]. pH varies from 0 to14, Mo precursor changes largely (14). Besides, pH affected the bonds between additives and nanoparticles during MoS$_2$ crystallinity process.

$$[\text{MoO}_4]^{2-} \rightarrow [\text{Mo}_2\text{O}_{24}]^{6-} \rightarrow [\text{Mo}_8\text{O}_{28}]^{4+} \rightarrow \text{MoO}_3 \cdot \text{H}_2\text{O}$$

(14)
The common used pH regulators were HCl [85], H₂SO₄, NH₃, H₂O [56] and NaOH. The effects of pH on products were investigated [34]. pH below 6.0, the products consisted of a little MoO₂ and MoS₂, pH above 7.5, the products were little MoO₂ as well as MoS₂ and much MoO₃, pure MoS₂ powder was obtained only when pH between 6.0 and 7.5. Mo conversion increased as the pH increased [77]. Ultrathin MoS₂ films with exposed layered structure were grown on fluorine-doped tin oxide (FTO) at pH=10 [68]. Flower-like MoS₂ was synthesized with high purity via hydrothermal at pH=6 [66]. Ammoniated MoS₂ was prepared with ammonia as the reaction medium [80]. MoS₂ nanorods were successfully prepared with sillicontungstic acid [90], the products were nanoparticle without sillicontungstic acid (hydrochloric acid or nitric acid), once sillicontungstic acid was added, the products were nanorods with uniform morphology. Nowadays, the application of pH regulators was limited to inorganic acids, organic acids were less. Compared with inorganic acids, the molecule of organic acids is larger and contains more functional groups. The application of organic acids affect the morphology of products and lead to the formation of metal dopants. Taking citric acid for example, which were applied to the synthesis of nanomaterial [52]. it not only can adjust pH, but also can play a role in reduction process.

Figure 9. Schematic illustration of different MoS₂ nanostructures [65]

4. Conclusions
The current researches of MoS₂ mainly concerned on electrical properties, the research of reaction system was relatively less. In this paper, the hydrothermal and solvothermal reaction system was divided into 6 parts, but not every part needed. The application of multifunctional raw materials can greatly simplify reaction system. Besides, low cost, stable and recyclable MoS₂ catalysts are also a direction for future research.

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